The Ecological Significance of Atrazine Effects on Primary Producers in Surface Water Streams in the Corn and Sorghum Growing Region of the United States (Part II).

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Office of Prevention, Pesticides and Toxic Substances
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# The Ecological Significance of Atrazine Effects on Primary Producers in Surface Water Streams in the Corn and Sorghum Growing Region of the United States (Part II)

## I. Executive Summary

As a condition of re-registration for atrazine in 2003, the US Environmental Protection Agency (US EPA) required Syngenta Crop Protection, Inc. to develop a monitoring program to determine whether atrazine concentrations in streams exceeded a level of concern (LOC) for aquatic plant communities. The goals of the Atrazine Ecological Exposure Monitoring Program (AEEMP) were to estimate the extent of watersheds with flowing waters that exceed atrazine LOC triggers for aquatic community effects and to characterize watershed attributes that can be used to identify other streams where atrazine exposures above the LOC are likely to occur. To address these goals, Syngenta monitored atrazine concentrations over time at 40 sites selected to statistically represent vulnerable watersheds in corn and sorghum producing areas.

The Agency adopted a general methodology for LOCs based on discriminating exposures that caused no or slight effects from those that caused significant effects in a set of 33 microcosm and mesocosm (cosm) studies. Because of the diversity of exposure time-series among cosms and in natural systems, this methodology requires an effects model that can provide a measure of severity (the Model Effects Index, MEI) for different exposure time-series and thereby support extrapolation of observed effects in cosms to natural systems. This effects model should be generic in that extrapolations among exposure time-series are not sensitive to physical/chemical/biological attributes of the ecosystems, because such attributes often will not be characterized and the effects of these attributes on responses to atrazine are not established. The registrant developed an atrazine-specific model for low-order streams in corn and sorghum growing areas from an existing aquatic community model (the Comprehensive Aquatic System Model, CASM) to provide the MEI for the general methodology. This CASMATZ model was not intended to simulate exact aquatic community responses in the various cosms and natural systems, but to serve as a means for relating atrazine exposure chemographs from monitoring to the results of the cosm studies. This is accomplished by assigning an LOC for the MEI based on the cosm data and using this LOC to assess MEIs calculated for exposure time-series observed in natural systems.

The US EPA presented its evaluation of the LOC approach and of the preliminary results of the AEEMP to the FIFRA Science Advisory Panel (SAP) in December 2007 (USEPA, 2007). The SAP provided feedback on the use of the CASM<sub>ATZ</sub> model to interpret monitoring results and the extent to which the methods could be used to determine the extent to which water bodies exceed atrazine thresholds of concern for aquatic community effects (FIFRA SAP, 2008). The SAP also provided recommendations on the Agency's planned approach to identify additional waters that

may exceed the atrazine LOC based on watershed characteristics of those sites that exceeded the LOC in the AEEMP study.

## A. Major Issues for Consideration at the May 2009 SAP Meeting

This document summarizes US EPA's progress since the 2007 SAP in response to comments from the Panel (FIFRA SAP, 2008). The Agency's preliminary evaluation of the version of CASM presented to the 2007 SAP (hereafter referred to as CASM<sub>ATZ1</sub>) found little sensitivity to the exposure start date and environmental variables and only moderate sensitivity to toxicity parameter selection (USEPA, 2007). Therefore, CASM<sub>ATZ1</sub> appeared to be suitable for the effects model in the desired generic methodology for establishing the LOC threshold for community-level effects, contingent on additional sensitivity analyses. Because of concerns about unrealistic seasonal dynamics of plant populations in CASM<sub>ATZ1</sub>, US EPA developed CASM<sub>ATZ2</sub> to address these issues. However, these changes resulted in considerable sensitivity to selections for toxicity parameters, exposure start date, and environmental variables.

Because of this sensitivity, the Agency believes that CASM is more suitable for site-specific applications for which it was originally developed than for the generic application for flowing water bodies desired here. Therefore, US EPA developed an alternative approach for the MEI based on the same plant toxicity sensitivity distributions used for CASM. Unlike CASM<sub>ATZ2</sub>, this "Plant Assemblage Toxicity Index" (PATI) method results in risk factors that are insensitive to uncertainties in its parameterization. The risk factors computed using the PATI-based MEI are close to the median risk factors from the default CASM<sub>ATZ1</sub> configuration and are well within the variability observed in the sensitivity analyses for the CASM-based MEIs. Because the generic CASM-based application would entail large uncertainties that would require considerable more work to define, US EPA proposes that the atrazine assessment methodology use a PATI-based MEI rather than a CASM-based MEI. This analysis is described in Section IV.

The US EPA used the PATI method to analyze the chemographs from the 40 monitoring sites in the AEEMP. The analysis found:

- 3 sites that exceeded the LOC in multiple years: MO-01, MO-02, NE-04
- 6 sites that exceeded the LOC in one year only: IN-05, IN-11, MO-03, NE-02, NE-05, NE-07
- 31 sites that never exceeded the LOC during the sampling period

The sites that exceed the LOC in multiple years represent approximately 9% (0 to 19% with 95% confidence limits) of the upper 20th percentile of vulnerable watersheds as identified by the USGS watershed model Watershed Regression on Pesticides (WARP). The sites that exceed the atrazine LOC no more than once in three years represent 14% (3 to 25%) of those vulnerable watersheds. Section V summarizes the monitoring analysis.

The US EPA compared atrazine use, land cover, soil, hydrology, and climate factors among watersheds for the AEEMP monitoring sites. Upstream catchment areas for monitoring sites that exceeded the atrazine LOC in multiple years had a relatively high proportion of soils with a high runoff potential (as defined by the USDA Runoff parameter or hydrologic soil group) and had a high percentage of soils with a shallow depth to a drainage restrictive layer.

The presence of runoff prone soils, as indicated by the USDA runoff class or hydrologic soil group, characterize sites that have the potential to exceed the atrazine LOC on occasion (symbolized by those sites that exceeded the LOC once in three years of sampling). The presence of soils with a shallow restrictive layer characterizes those sites that exceed the LOC in multiple years. In Section VI, the Agency identified additional watersheds that may be similarly vulnerable to high atrazine exposures based on the following characteristics:

- Upstream catchment areas comprised of at least 40 percent soils with a very high or high runoff potential or at least 60 percent hydrologic group C or D soils, and,
- At least 45 percent of the catchment area consists of soils with a subsurface layer that has a saturated hydraulic conductivity less than 1 µm/s within 50 cm of the surface.

These conditions occur in areas where

- Atrazine use intensity within the catchment is at least 0.1 lb ai/ acre or corn or sorghum occupies at least 10 percent of the catchment, and
- Average annual rainfall is at least 23 inches or average April-May precipitation is 6 inches.

# **B. Charge Questions**

Based on the analyses presented in this document, the US EPA will present the following charge questions to the SAP:

The foundation of the US EPA methodology for specifying levels of concern (LOCs) for atrazine exposures in natural freshwater systems is the relationship of atrazine exposure to effects on aquatic plant community structure and function in microcosm and mesocosm (cosm) studies. Comparing effects among the different atrazine exposure time-series in the cosm studies and extrapolating effects to other exposure time-series in natural systems requires an effects model that can be applied to any exposure time-series to provide a consistent, quantitative index for toxic effects on the plant community (Model Effects Index, MEI). MEI values for cosm exposures are used to develop an LOC for the MEI (LOC<sub>MEI</sub>) that best discriminates between cosm exposures with and without significant effects. MEI values for exposures in natural systems can then be evaluated relative to this LOC<sub>MEI</sub>.

(1) The effects models considered in this document require effects concentrations (ECs) from single-species plant toxicity tests with atrazine that

are consistent with respect to the nature and magnitude of the toxic effects. Reports on and reviews of such tests provide ECs that vary widely in meaning, so a new review was conducted and test results were used to develop a compilation of plant specific growth rate vs concentration relationships (Section IV.B). Please comment on the strengths and limitations of this review and synthesis of plant toxicity tests for providing toxicity sensitivity distributions for use in the atrazine assessment methodology.

- (2) One source considered for the desired MEI is the Comprehensive Aquatic Systems Model (CASM), a community simulation model. In response to a previous SAP review, this model was modified to give a more realistic, dynamic simulation of a midwestern stream (CASM<sub>ATZ2</sub>). Sensitivity analyses for this revised model were conducted, including some additional analyses suggested in the previous SAP review. These analyses indicated considerable sensitivity of risk determinations to the selection of species toxicity parameters and to various physicochemical variables (Section IV.C). This indicates that CASM<sub>ATZ2</sub> is more suitable for a site-specific, data-intensive assessment than the generic application that is desired for these atrazine assessments. Please comment on the advisability and value of using CASM<sub>ATZ2</sub> for generic assessments given these findings and on the nature and feasibility of additional development efforts that would be needed to implement this model.
- (3) An alternative source considered for the desired MEI was an index of the severity of toxic impact on a plant assemblage (Plant Assemblage Toxicity Index, PATI) based directly on single-species plant toxicity relationships (Section IV.D). Please comment on the merits and limitations of this source for the MEI. Based on the coherence of risk evaluations between the PATI-based and the CASM-based methodologies, EPA has concluded that the additional processes included in CASM are not needed for the assessment methodology and that the PATI-based methodology should be adopted. Please comment on the merits of this conclusion.

The Agency identified three sites that exceeded the PATI LOC<sub>MEI</sub> in multiple years and six sites that exceeded the LOC<sub>MEI</sub> in one year (Section V). Based on the results of the Agency's watershed analysis in Section VI to identify additional sites that might exceed the atrazine LOC, US EPA proposes two questions for the SAP:

(4) Based on an analysis of watershed characteristics of the 40 monitoring sites, the US EPA concluded that the presence of soils that either have a high runoff potential or are in hydrologic soil group C or D, and have a shallow layer with a moderately low saturated hydraulic conductivity best distinguish sites that exceed the LOC in multiple years from those that do not exceed the LOC. Please comment on the merits of the watershed criteria the Agency used to identify watersheds that might exceed the atrazine LOC.

(5) Neither atrazine use intensity nor rainfall data (annual or monthly) correlate positively with watersheds that exceed the LOC. The Agency noted that the monitoring site selection already focused on areas with sufficient atrazine use to potentially result in high atrazine exposures in streams. Please comment on the Agency's proposed approach to establish a minimum criteria for atrazine use intensity ( $\geq$  0.1 lb ai/A) and rainfall (>23 inches annually).

#### II. Introduction

In January, 2003, the US Environmental Protection Agency (US EPA) issued an ecological risk assessment as part of the Interim Registration Eligibility Decision (IRED) for atrazine (US EPA, 2003a). As a condition of re-registration, the atrazine registrants were required to develop a monitoring program to determine whether atrazine concentrations in streams associated with corn and sorghum production were exceeding a designated effects-based threshold. This threshold was based on aquatic plant community effects. If this threshold is exceeded, then a watershed-based mitigation program would be required.

In December 2007, the Agency summarized its preliminary review and interpretation of the initial results of the Atrazine Ecological Exposure Monitoring Program (AEEMP) before the Federal Insecticide, Fungicide, and Rodenticide (FIFRA) Scientific Advisory Panel (SAP). The Panel provided feedback related to the interpretation of the results and the extent to which the methods used by the Agency could be implemented or adapted in any future atrazine aquatic assessments or monitoring efforts to determine the extent to which water bodies exceed atrazine thresholds of concern for aquatic community effects.

The purpose of this May 2009 meeting is to update the SAP on the issues that were raised in the December 2007 Panel Meeting and to present additional science issues that have developed as a result of the subsequent analyses.

## A. Regulatory Background: 2003 IRED and MOA

Atrazine, a triazine herbicide used against broadleaf and some grassy weeds first registered for use in 1958, is now estimated to be one of the most widely used herbicides in the United States. Atrazine inhibits primary production by reversibly blocking photosynthesis. It is both mobile and persistent in the environment. Predominant use is on corn and sorghum.

The US EPA completed its evaluation of the registration of atrazine, culminating in the IRED in January 2003 (US EPA, 2003a), which identified risk to aquatic plant communities as the principal ecological concern from continued atrazine use. The IRED and a memorandum of agreement (MOA) with Syngenta Crop Protection, Inc (Syngenta), the registrant of atrazine (US EPA, 2003b) provided a "roadmap" for addressing the uncertainty associated with ecological risk concerns<sup>1</sup>.

A key element of the IRED was aquatic plant communities as the principal ecological risk concern from atrazine use. Numerous toxicity tests with a variety of plant and animal species have shown aquatic plant growth to generally be much more sensitive to atrazine than are various effects on aquatic animals. At comparable

<sup>&</sup>lt;sup>1</sup> Potential human health issues associated with exposure to atrazine are being addressed separately as part of the IRED/MOA process and are not discussed in this report.

percentages in these cumulative distributions, plant growth is circa 3-10 times more sensitive than chronic endpoints for animals and circa 20-100 times more sensitive than acute toxicity to animals (IRED 2003). Aquatic plant communities as a whole were of concern, as opposed to effects on individual species, because of issues related to the rapid, reversible nature of small to moderate effects of atrazine on plant growth, the influences of competition and compensation within the community, recovery rates of community perturbations, and the seasonality of community sensitivity. Thus, an analysis of the atrazine microcosm and mesocosm (cosm) studies was undertaken to base the ecological level of concern (LOC) on aquatic plant communities. Atrazine has been the subject of many cosm studies. The durations of these studies ranged from a week to a year at exposure concentrations ranging from 0.1 to 10,000 µg/L. Most of the studies have focused on atrazine effects on phytoplankton, periphyton, and macrophytes; however, some also included measurements on animals. Based on these studies, the IRED identified the LOC for recurrent or prolonged exposures to atrazine to be 10 to 20 µg/L, but did not address how this LOC might depend on the diverse exposure profiles (i.e., atrazine concentration time-series) present in the cosm studies and in natural freshwater systems.

As a condition of re-registration, the Agency required atrazine registrants to develop a monitoring program to determine whether atrazine concentrations in streams associated with corn and sorghum production were exceeding a designated effects-based threshold. The Agency required the atrazine registrants, in consultation with the US EPA, to develop a program under which the registrants would monitor for atrazine concentrations and take measures to lower these exposures if such action is necessary. The AEEMP focused on stream systems within a watershed context (US EPA, 2003a, 2003b).

Based on the 2003 ecological risk assessment for atrazine, the Agency identified several key items to be addressed in the design of the monitoring study (US EPA, 2003b). These items resulted in the following study objectives required to meet the US EPA's needs under FIFRA.

- 1) Identify aquatic community-level thresholds of concern based on available microcosm and mesocosm studies (cosm studies) and develop a method that relates these aquatic community responses to atrazine exposure profiles in a reasonable and transparent manner.
- Design a monitoring program to estimate the extent of watersheds in corn and sorghum producing areas that have flowing waters which exceed atrazine LOC triggers for aquatic community effects.
- 3) Based on results of the monitoring study, identify watershed attributes that can be used to identify other watersheds where these higher atrazine exposure areas are likely to occur.

#### B. October 2003 Addendum to IRED

An October 31, 2003, addendum to the January 2003 IRED specified the key questions the Agency wanted the monitoring study to address, outlined the methodology for determining the LOC trigger, and briefly described the monitoring study design and proposed protocol submitted by Syngenta (US EPA, 2003b).

In this addendum, a new approach for setting a LOC was proposed. As in the original IRED, the LOC trigger was based on results of cosm studies. The set of cosm data was expanded to include 33 separate studies with 77 separate atrazine exposures (US EPA 2003c). The severity of atrazine effects on the aquatic primary producer plant community observed in the each exposure were scored based on five effect classes developed by Brock *et al.* (2000):

- 1 = no effect
- 2 = slight effect
- 3 = significant effect followed by return to control levels within 56 days
- 4 = significant effect without return to control levels during an observation period of less than 56 days
- 5 = significant effect without return to control levels for more than 56 days

The Agency designated discrimination of cosm studies with Brock scores of 3 to 5 from 1 to 2 to provide the basis for establishing the LOC.

In addition to this formalization of cosm descriptions, the proposed new approach for setting a LOC addressed how LOCs should vary among diverse exposure profiles. The approach adopted for this was to use a aquatic community simulation model to assign a measure of severity for the impact of each exposure profile, to determine an LOC for this modelled measure of severity that best discriminated the Brock score groups, and then to determine it this LOC was exceeded by the exposure profiles in natural aquatic systems of interest (US EPA 2003c). As such, the LOC does not rely on the model to provide absolute predictions of community dynamics or atrazine effects in any particular system, but rather a measure of severity that is informative of the relative effects of different exposure profiles. Thus, LOCs are still tied to the absolute levels of effects observed in the cosm studies. The model used was the Comprehensive Aquatic Systems Model (REFS), or CASM, which was adapted to describe atrazine effects in a 2<sup>nd</sup>- to 3<sup>rd</sup>-order stream representative of those in the midwestern U.S. corn- and sorghum-growing regions (Volz et al. 2007), this version being designated here as CASM<sub>ATZ1</sub>.

The AEEMP measured atrazine concentrations for at least two years at 40 monitoring sites representing watersheds associated with corn and sorghum production that are vulnerable to atrazine exposure in streams according to the USGS Watershed Regression on Pesticides (WARP) model (US EPA, 2007). The intent of the monitoring study was to both determine the extent to which streams exceed the atrazine LOC for aquatic community effects and to identify other areas within the atrazine use area where LOCs may be similarly exceeded.

The next step in the assessment involved designing a monitoring program that generated exposure profiles (chemographs) sufficient to assess the magnitude, duration, and frequency of atrazine exposures, given the potentially flashy nature of atrazine exposure in stream systems. Because the LOC trigger reflects both magnitude and duration of exposure, the chemograph must reflect sampling at a sufficient frequency to characterize atrazine exposure in flowing waters. Syngenta monitored 40 sites for at least 2 years based on a probability-based survey design that sampled 1,172 vulnerable watersheds deemed to most vulnerable to atrazine runoff. More detail on the monitoring program may be found in the 2007 SAP report (US EPA, 2007) and in Section V of this report.

#### C. December 2007 SAP Review

In the December 2007 SAP Meeting, the Agency discussed the preliminary development of an ecological LOC methodology and presented an analysis of the monitoring program using that model. LOC development included a summary of the underlying approach to relate effects from time variable real world exposure to aquatic plant community effects found in the cosm studies using an aquatic community-level model (CASM<sub>ATZ1</sub>). The SAP document included a preliminary sensitivity analysis of CASM<sub>ATZ1</sub>, results of the ecological stream monitoring from 2004 to 2006, identification of sites that exceeded the CASM<sub>ATZ1</sub>-based LOC with associated population statistics, and a proposed GIS-based approach for extrapolating results from the 40 watersheds to all watersheds where atrazine is used.

The SAP issued its evaluation and recommendations on March 5, 2008 (FIFRA SAP, 2008). In that report, the SAP concurred with the conceptual approach of using a community simulation based model to relate time variable exposures to community-level effects data represented by the cosm data. The SAP also made several recommendations for the Agency to pursue before implementation of the CASM based approach. These recommendations included:

- Undertake further evaluation of CASM;
- Re-emphasize the concept that the CASM approach is intended not to simulate exact aquatic community responses but to serve as a bridge between atrazine exposure chemographs from monitoring to the results of the cosm studies; and
- Determine the extent to which atrazine levels in water bodies exceed the aquatic community-level LOCs, including:
  - Interpretation of the monitoring results and identification of chemographs that exceed the LOC, and
  - o Identification of the location of other watersheds with characteristics similar to those that exceeded the LOC in the monitoring study.

## D. May 2009 SAP Review

This document summarizes work that has been completed since the 2007 SAP in response to comments from the Panel (FIFRA SAP, 2008). The Agency believes that it has addressed the concerns of the 2007 SAP and has charted a path forward to identify the concentrations and durations of atrazine in flowing water bodies that may cause risk to aquatic plant communities and to identify where other water bodies with similar vulnerability characteristics as those monitored may be located.

The Agency has addressed the SAP's recommendations for community modeling, site monitoring, and extrapolation of results to all atrazine bearing waters. The Agency is consulting with this SAP on scientific issues related to the interpretation of the results of the monitoring program and the extent to which the methods used by the Agency could be used or adapted in any future atrazine aquatic assessments or monitoring efforts to determine the extent to which water bodies exceed atrazine thresholds of concern for aquatic community-level effects. The Agency also has posed questions for the SAP on these issues which follow in each of the detailed sections below.

This document covers the following topics:

- The purpose of the assessment;
- An evaluation of the cosm studies used to develop the Level of Concern (LOC) (Section III);
- A more complete description of the general strategy for evaluating ecological LOCs for atrazine in freshwater systems (Section IV-A).
- An analysis and new compilation of single-species plant toxicity tests that provides information needed for effects models (Section IV-B).
- A revised version of CASM (CASMATZ2) and a new sensitivity analysis using CASM<sub>ATZ2</sub> based on comments from the 2007 SAP (Section IV-C);
- A proposed alternative to CASM<sub>ATZ2</sub>, the Plant Assemblage Toxicity Index (PATI) based directly on single-species plant toxicity data (Section IV-D);
- An update of the monitoring data and results of 2004 to 2008 data relative to both CASM<sub>ATZ2</sub> and PATI-based approaches for determining the LOC (Section V);
- An evaluation of watershed characteristics of the atrazine monitoring sites with the intent of identifying those characteristics that distinguish between sites that exceed the LOC and those that do not exceed the LOC (Section VI-B); and
- A GIS-based approach to identify additional watersheds within the atrazine use area with characteristics similar to those that exceed the LOC in the AEEMP study (Section VI-C).

## III. Analysis of Atrazine Micro- and Mesocosm Studies

The Agency's LOC is based on the results from 33 atrazine cosm studies, which were considered as part of the 2007 SAP (USEPA, 2007). Since the 2007 SAP, the US EPA reviewed the 33 cosm studies to confirm Brock score assignments and develop associated atrazine exposure profiles. The results of this analysis are provided in Appendix III-1. An atrazine exposure profile, associated Brock score, and description of the magnitude of effect is provided for each data point. Further details on confirmation of the Brock scores and development of the atrazine exposure profiles for each of the associated endpoints are provided below. Because this analysis was based on cosm studies considered in the 2007 SAP and the Panel concurred on the use of data from these studies to establish the LOC, there are no specific charge questions associated with the updated review of cosm data points.

#### A. Review of COSM Data Points and Associated Brock Scores

US EPA reviewed each of the 33 atrazine cosm studies in order to document the observed effects, the magnitude of effect, time to recovery (if applicable), and the associated Brock score. Effects observed in the cosm studies included changes in aquatic plant biomass, chlorophyll a concentration, photosynthesis rate (<sup>14</sup>C uptake, oxygen production), and shifts in aquatic plant community structure relative to a control.

This review confirmed the Brock scores for 71 of the original 77 data points (~92%). Six of the Brock scores were revised, and an additional data point was added. Four of the six Brock score revisions resulted in changes from either 1 to 2 or 3 to 4 and had no impact on the LOC determination because Brock scores of 1 and 2 are grouped together and 3, 4, and 5 are grouped together. For the other two data points, the original Brock scores of 2 were revised to 3 or 4. The additional data point had a Brock score of 2. As discussed further in Section IV-D-5, the impact of the Brock score revisions on the distribution of data points with significant effects versus those with slight or no effects is minimal. The revised Brock scores and additional data point are documented in the "Comments" column of Appendix III-1 and are summarized in Table III-1.

Citation	Data Point No. in Excel Summary Spreadsheet	Change	ata Point Changes  Basis for Change		
DeNoyelles et al (1989)	52	Brock score changed from 2 to 3	A 50% decline in phytoplankton and biomass production was observed at a nominal atrazine concentration of 20 ug/L compared to the control, with recovery occurring at 3 weeks. The Brock score for this data point was initially identified as 2 meaning that the effect was "slight" and/or "transient". Given that a significant decline in biomass was observed (50%) and that recovery of biomass occurred at 3 weeks, the Brock score for this data point		
Lampert et al. (1989)	58	Data point added (0.1 ug/L) with a Brock score of 2	was changed to 3.  The data point associated with 1 ug/L based on reduction in primary production via photosynthetic rate was changed to 0.1 ug/L. This endpoint was evaluated only at 0.1 ug/L treatment level.		
	58b	Brock score changed from 2 to 4	An atrazine concentration of 1 ug/L resulted in approximately 70% to 80% reduction in oxygen levels relative to controls, without any observed recovery for the full duration of the 18-day study. These results are consistent with a Brock score of 4 (clear effect, without recovery for a study <56 days); therefore, the Brock score for this data point was changed from 2 to 4.		
Brockway et al., 1984	39 and 40	Brock score changed from 3 to 4	A Brock score of 3 was previously assigned for this data point, which means that there was a clear effect with recovery within 56 days. Although recovery occurred in the continuous flow experiments that were associated with removal of atrazine from the test system, no recovery occurred in the static experiments. Therefore, the results of this study are consistent with a Brock score of 4. This change will not affect the LOC determination.		
Moorhead and Kosinski, 1986	46	Brock score changed from 3 to 4	Effects on community productivity were observed at the end of the 7-day study. Therefore, recovery did not occur during the study duration, which was less than 56 days. These results are consistent with a Brock score of 4. This change will not affect the LOC determination.		

Citation	Data Point No. in Excel Summary Spreadsheet	Change	Basis for Change
Stay et al., 1989	50	Brock score changed from 3 to 4	A decrease in primary productivity was observed for the entire 42-day study. Therefore, recovery did not occur during the study duration, which was less than 56 days. These results are consistent with a Brock score of 4. This change will not affect the LOC determination.
Brockway et al., 1984	66	Brock score changed from 1 to 2	Oxygen production was slightly reduced from Days 10 to 45. Oxygen production was typically within 90% of controls, but was approximately 80% of controls for about 7 days during the first month of the study. These results show a slight and/or transient effect, which is consistent with a Brock score of 2. This change will not affect the LOC determination.

#### **B. Atrazine Exposure Profiles in the Cosm Studies**

In the original evaluation of CASM presented to the SAP in 2007, the data point exposures were defined by a single atrazine concentration over the duration of the data point. This approach did not account for dissipation of atrazine within the cosm test systems but assumed exposure was constant over the full duration of the study. In the single exposure studies, atrazine exposures degrade over time in the aquatic systems.

To address this inconsistency, the Agency reviewed the atrazine exposure profiles for each of the cosm studies to develop a specific chemograph exposure profile for each of the data points. For 21 of the 78 data points, the exposure profile was based on a constant exposure. For the remaining 57 data points, the exposures varied with declining concentrations over the duration of the study. For test systems associated with these data points, the US EPA developed study-specific chemographs from one of three methods depending on the availability of data:

- (1) the reported (measured) time-series concentrations;
- (2) the reported starting concentration and a study-specific dissipation half-life; or
- (3) a generic dissipation half-life of 165 days from the average of half lives reported in the other studies.

Appendix III-1 links the atrazine exposure profiles, provided in separate worksheets, to each of the 78 data points. A review of the cosm studies resulted in substantial changes in the duration of one study. While the entire study duration for Brockway et al. (1984) was 70 days, the exposure profile was complex. For example, the 0.5-ug/l treatment level (data point #65 in Appendix III-1) lasted for only 29 days; subsequent exposures increased and decreased at various intervals ranging from

nominal atrazine concentrations of 0 to 100 ug/L. The US EPA made the following changes in Appendix III-1 to more accurately reflect the actual exposure durations for the data points in the Brockway et al. (1984) study:

Data Point #39: Duration changed from 70 days to 55 days Data Point #40: Duration changed from 70 days to 15 days Data Point #65: Duration changed from 70 days to 29 days

The US EPA used the revised Brock Scores and exposure profiles for the 78 endpoints in the LOC determination further discussed in Section IV. The Brock score revisions were minor (only 2 out of 78 endpoints shifted from a "slight or no effect" category to a "significant effect" category). Changes in the exposure profiles, shifting from a single nominal concentration over the duration of the study to concentration profiles that reflect the decline in atrazine concentrations that occurred over the duration of the study would likely have a greater impact on the net exposures of the longer-duration studies than those of short-duration. However, these changes reflect more realistic exposures over the duration of the study, reducing uncertainty introduced by errors in exposure estimates. A comparison of the cosm data plotted in Figure IV-1 with a similar plot in the 2007 SAP document (USEPA, 2007) shows little change in the distribution of data points with significant effects versus data points with slight or no effects as a result of the end point changes documented in this section.

# IV. Method for Assessing Ecological Levels of Concerns for Atrazine Exposures in Freshwater Systems

This section addresses methods for assessing ecological LOCs for atrazine exposures to freshwater systems. First, the problem being addressed is defined and a general strategy for the assessment methodology is presented. Second, toxicity test data for individual plant species are reviewed and summarized for use in this methodology. Third, the use of the community simulation model CASM in the methodology is described and evaluated. Fourth, a direct application of atrazine toxicity data as an alternative to CASM is described and evaluated. EPA proposes using this alternative in the methodology rather than CASM because it provides similar results with less uncertainty and less complexity, and appears to be more suited as a generic application for assessing atrazine concentrations in streams.

# A. Problem Definition and General Strategy

#### 1. Problem Definition

As discussed earlier, a set of microcosm and mesocosm (cosm) studies with atrazine serve as the foundation for determining LOCs for atrazine exposures in natural freshwater systems. Figure IV-1 summarizes these data (updated per Section III compared to the December 2007 SAP review).

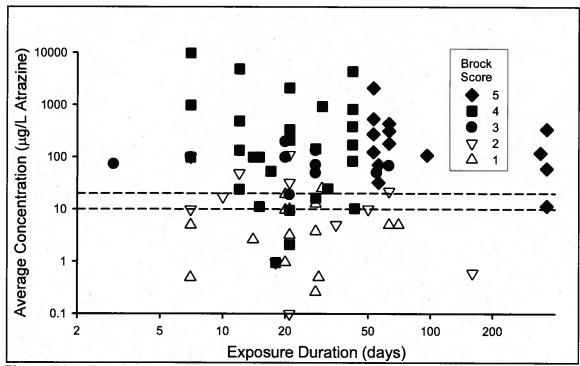


Figure IV-1 Brock scores in atrazine cosm exposures as a function of exposure duration and average concentration. Dashed lines denote the 10-20  $\mu$ g/L LOC concentration range designated by the 2003 IRED.

Each datum on Figure IV-1 is characterized by the exposure duration at which effects were assessed, the average exposure concentration over this duration, and an effects score (Brock score) using the system of Brock et al. (2000) as described in Section II. A fundamental assumption in using these cosm data is that they collectively describe a relationship of effects to exposure that is relevant to natural freshwater systems. In other words, natural aquatic plant communities will react adversely if subjected to the same exposures that elicited significant adverse effects in the cosm studies. This assumption is inherent in any assessment that extrapolates toxicity experiments to the field. The use of experimental ecosystems arguably provides a better basis for such extrapolations than do single-species toxicity tests.

An important consideration in using the cosm data to establish LOCs is the diversity of exposure concentration time-series. Not only do the cosm studies have different durations, but the exposure concentrations within these durations can range from being roughly constant to declining substantially with a half-life as short as 3 days (Section III). This variability makes if difficult to compare effects among different cosm studies, but exposure variability is an even greater problem for extrapolating these effects to the field. For natural freshwater systems, atrazine exposures tend to be even more variable than in the cosms and do not have a fixed duration. Atrazine enters natural freshwater systems largely in rainfall-driven runoff, resulting in highly variable and episodic exposures (Figure IV-2) that depend on rainfall distribution, atrazine application patterns. topography, and soil properties. Therefore, a primary goal for this assessment methodology is to address the diversity of exposure time-series both in the experimental cosms and natural systems. The cosm data do not provide sufficient information for defining such time effects because the scoring system is semiquantitative and the study conditions and responses do not fully address the issues of duration and time-variability. Thus, another issue facing this methodology is to base time effects on considerations other than the cosm data.

As was discussed in Section II, LOCs are based on discriminating the Brock score group of 3 to 5 (i.e., significant effects) from the score group of 1 or 2 (i.e., no to slight effects). As shown in Figure IV-1, these two score groups are largely separated, although some overlap also exists, particularly over the 10-20  $\mu g/L$  range.. Some of this overlap is due to the exposure time-variability issue (which cannot be fully addressed in the two-dimensional graphic format of Figure IV-1); for example, the two lowest squares involve exposures with fast decays, so that the plotted average exposure concentrations are much lower than the peak concentrations. However, this overlap is also reflective of other differences among the cosms. Unfortunately, these differences are not sufficiently understood to support methods for better discriminating the score groups. In any event, this overlap means that any LOC methodology will need to address the occurrence of false negatives (i.e., Brock scores of 3 to 5 which lie below the LOC) and false positives (i.e., Brock scores of 1 or 2 which lie above the LOC).

The positioning of the LOC relative to the number of false positives and negatives is a key risk management decision.

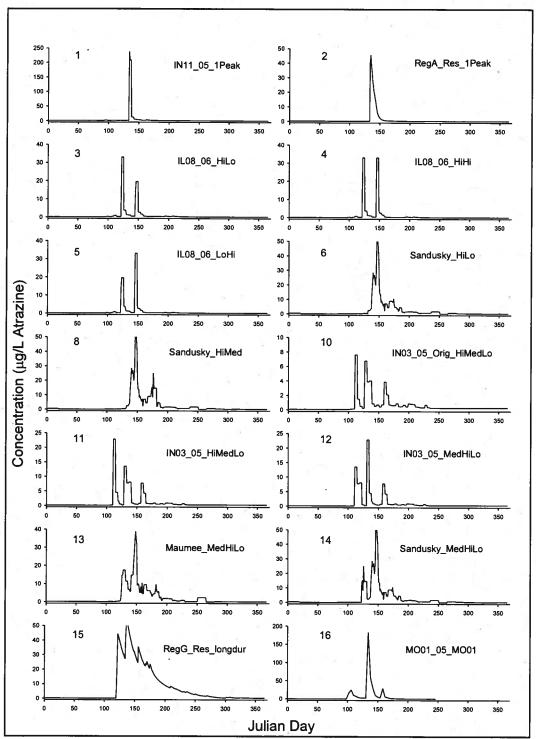


Figure IV-2 Examples of atrazine exposure time-series for natural freshwater systems. These chemographs, created for sensitivity analyses of proposed methodologies in Sections IV.C and IV.D, were intended to span the diversity of exposures that might occur in natural systems. Chemographs were obtained from monitoring data

described in Sections V and VI. Chemograph numbers 7 and 9 are not shown because they are identical to numbers 6 and 8, respectively, except shifted to two weeks earlier to evaluate timing of exposure.

To illustrate this decision, Figure IV-1 shows horizontal lines at 10 and 20  $\mu$ g/L (the LOC range specified in the 2003 IRED (U.S.EPA, 2003a)). The upper line corresponds to false positives and false positives being about equal, while the lower line has considerably more false positives than negatives. It is important to emphasize that these horizontal LOC lines are presented here only to illustrate the concept of using the cosm data to position the LOC, and that the methods described in this document will not produce simple, fixed-concentration LOCs.

Therefore, the general problem is to extrapolate effects observed under one exposure time-series to another time-series. This extrapolation will allow effects observed for different cosm exposures to be compared and synthesized into an LOC, and for this LOC to be used to assess the types of exposures observed in natural systems. For example, if 20  $\mu$ g/L atrazine is an LOC for a 60-day constant exposure, what would be the LOC for a 30-day constant exposure? Or what would be the LOC based on the highest peak (or some average concentration) for a chemograph with a complex shape, such as those in Figure IV-2?

The LOC thus must be a function that can be computed for the entire range of exposure time-series encountered in cosm studies and in natural freshwater systems of interest. This requires a model that can provide, for any exposure time series, a comparable, quantitative measure of expected effects, which will be referred to as the model effects index (MEI). For example, this might be a model-calculated percent reduction in total plant biomass over a specified duration.<sup>2</sup> By correlating the MEI to the Brock scores for the various cosm exposures, an LOC for this MEI (LOCMEI) can be determined, so that the LOC is on a modeled effects scale rather than on a concentration scale. Evaluation of the exposure time-series in natural freshwater systems is then simply done by computing the MEIs for these time-series and comparing them to the LOC<sub>MEI</sub>. One consequence of such a "calibration" of the LOC<sub>MEI</sub> to the cosm data is that the model is not required to make absolute predictions of effects in an actual aquatic system, but rather is used to support comparisons of the relative severity of different exposures time-series. This general strategy for assessments is described in further detail in Section IV.A.2 and specific options for the MEI are addressed in Sections IV.C and IV.D.

Because the cosm data do not contain sufficient information on time-dependence of effects, this model also must provide an acceptable basis for this time-dependence. In addition, the model should provide extrapolations among

<sup>&</sup>lt;sup>2</sup> For the December 2007 SAP, the principal MEI used was the year-long average percentage reduction in the Steinhaus Similarity Index based on CASM simulations with and without an atrazine exposure.

different exposure time-series that are not adjusted for physical, chemical, and biological properties attributes (other than the exposure time-series) of the cosms and natural systems of interest. Even if a model is a function of such attributes, it must be applied with generic values for the attributes because there is insufficient empirical information on the relationship of effects to such system attributes to validate model predictions and because the model must be applicable to systems for which these system attributes are not defined. With the exception of exposure variability, the influence of system attributes on differences among cosm studies and on extrapolations from cosm studies to natural systems cannot be addressed.

# 2. General Strategy for Assessment Methodology

This subsection describes the general strategy for atrazine assessments in terms of two major steps: (1) establishing an  $LOC_{MEI}$  based on cosm data and (2) using the  $LOC_{MEI}$  to evaluate exposure time-series for natural freshwater systems. This general strategy can accommodate MEIs of widely different natures and is described here without specifying the exact nature of the MEI. However, for illustrative purposes, it is useful to provide actual values for some variables, so some calculations were made for the description. The effects model is only characterized as being able to convert an exposure time-series into a time-series of "percent effects". The MEI is set to the maximum 90-day average of these daily percent effects, this 90-day assessment period being an arbitrary example. The  $LOC_{MEI}$  is determined by equalizing false positives and negatives, and the  $LOC_{MEI}$  value is for illustrative purposes only.

#### Establishing a LOC<sub>MEI</sub> Based on Cosm Data

- (1) The MEI is determined for each of the atrazine exposures in the cosm data set. This MEI must be for a fixed **assessment period** to provide comparability among different exposures (i.e., effects confined to a short exposure period cannot be equated to effects extending over a longer exposure period; rather, average effects of each exposure over the same period should be compared). The selected assessment period must be appropriate to the nature of the MEI, the cosm studies, and risk assessment goals, and its selection is addressed in Sections IV.C and IV.D.
- (2) The observed Brock scores (1 through 5) for each cosm treatment are correlated to their respective MEIs, to determine what levels of the MEI are associated with observed effects in the cosm. An LOC<sub>MEI</sub> is determined that best discriminates between the score groups (i.e., 1 or 2 vs. 3 to 5), based on a desired relative incidence of false positives and negatives. Note that the LOC is now on the modeled effects scale rather than an exposure concentration scale.

Figure IV-3 depicts this process. The top panel shows the cosm data and highlights one of the data points, whose exposure time-series is shown in the left

middle panel. The effects model converts this exposure data to daily percent effects in the right middle panel and these daily values are in turn processed into 90-day running averages for this example. The MEI is set to the maximum (9.3%) of these running averages. In the lower panel, the Brock scores versus the MEIs are plotted for all of the cosm treatments. The LOC<sub>MEI</sub> is set to the MEI value that equalizes false positives and negatives (vertical line at 1.9%).

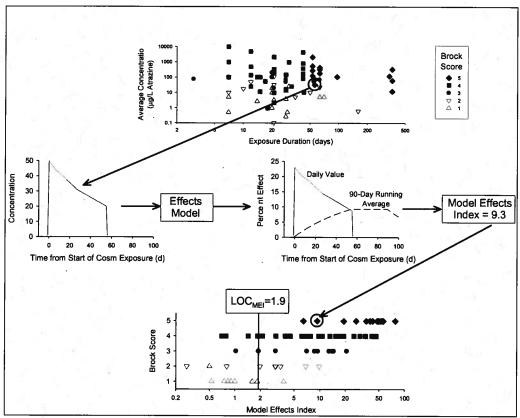


Figure IV-3 Strategy for establishing the level of concern for a model effects index based on cosm data

# Using a LOC<sub>MEI</sub> to Evaluate Exposure Time-Series from Natural Freshwater Systems

- (3) For each exposure time series from natural freshwater systems of interest, the MEI is calculated and compared to the  $LOC_{MEI}$  to see if it is exceeded, and by how much.
- (4) If desired, iterative model calculations can be conducted to determine the factor (*"risk factor"*) by which the exposure concentration time-series would need to be decreased for the MEI to exactly equal the LOC<sub>MEI</sub>, thereby providing further information for risk assessment.

Figure IV-4 depicts this process. The top left panel provides an example field exposure time-series. The effects model converts this exposure data to daily

percentage effects in the top right panel and these daily values are in turn processed into 90-day running averages, the maximum of which (6.3%) is the MEI. In this case, the MEI substantially exceeds the  $LOC_{MEI}$  (1.9% average effect). The bottom panels illustrate the process by which a risk factor can be determined. The model is iteratively applied to scale the exposure time-series (left bottom panel) so that the MEI exactly equals the  $LOC_{MEI}$  (right bottom panel). The ratio of the original exposure time-series to the adjusted one equals the risk factor, which is 3.5 in this case.

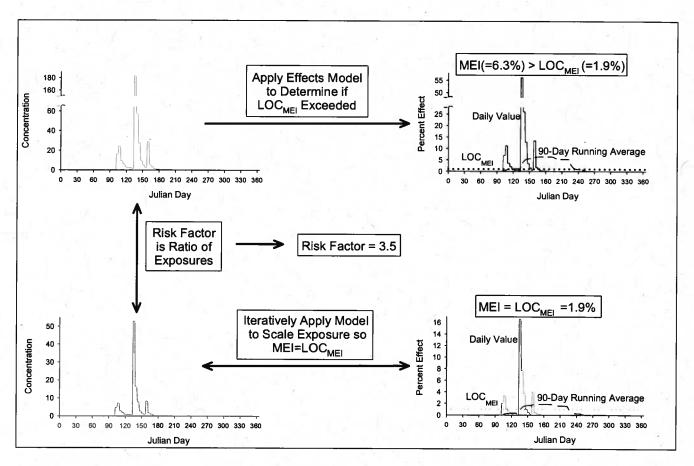


Figure IV-4 Strategy for using the level of concern for a model effects index to evaluate field exposures

For an exposure time-series of this exact shape, the bottom left panel of Figure IV-4 defines an LOC on a *concentration scale* basis, and the original exposure time series would need to be reduced by 3.5-fold to be at the LOC. This concentration-based LOC can be characterized by any single (e.g. the peak) concentration or any average concentration over the time-series, but if the relative shape of the time-series changes, this concentration-based LOC would not be valid and new model calculations would be needed to determine when exposure is at the LOC<sub>MEI</sub>.

## **B. Individual Plant Species Toxicity**

Options for the MEI that are evaluated in Sections IV.C and IV.D require information on the toxicity of atrazine to individual plant species. However, existing compilations of atrazine toxicity values (e.g., Giddings et al. 2000) have certain shortcomings regarding their applicability to the MEIs, which warranted reanalysis of existing single-species toxicity tests. This section describes the shortcomings of concern, summarizes the new review and analysis of toxicity data, and presents a new compendia of toxicity information more suitable for use in the MEIs. More details regarding the analyses are provided in Appendix IV-1.

Effects concentrations (ECs) from plant toxicity tests can vary widely in both value and meaning depending on how tests are conducted and analyzed. For microalgae, tests are usually conducted on cell suspensions under favorable (at least at test start) conditions of temperature, light, and nutrients. Measurement endpoints in such tests can vary, including actual biomass (wet or dry weights); surrogates for biomass such as cell counts, cell volume, optical density and chlorophyll content; and indicators of net photosynthesis such as oxygen evolution and radioactive carbon fixation. The period over which measurements are made can vary from less than an hour to several weeks, and measurements might be taken at multiple times or only at the end of exposure. Biomass or biomass surrogates might be analyzed based on gross values, net growth, area under the time-series of net growth, and/or specific growth rate (SGR)<sup>3</sup>.

The meaning of an EC can be greatly affected just by test duration and on whether it is based on gross biomass or net growth or SGR. Consider a toxicity test in which exponential growth is maintained so that the SGR is constant at any toxicant concentration and consider example values of 1/day and 2/day values for the SGR under control conditions (SGR<sub>C</sub>). If a particular toxicant concentration is an EC<sub>50</sub> for the SGR, the fraction reductions in gross biomass ( $p_G$ ) and net growth ( $p_N$ ) are:

$$p_G = 1 - \frac{e^{0.5 \square SGR_C \square}}{e^{SGR_C \square}}$$
  $p_N = 1 - \frac{e^{0.5 \square SGR_C \square} - 1}{e^{SGR_C \square} - 1}$ 

Therefore, for net growth, the concentration that is an EC<sub>50</sub> for SGR will be an EC<sub>62</sub> at 1 day, an EC<sub>73</sub> at 2 days, and an EC<sub>88</sub> at 4 days if the control SGR is 1/day, and an EC<sub>73</sub>, an EC<sub>88</sub>, and an EC<sub>98</sub>, respectively, at these times if the control SGR is 2/day. For gross biomass, the respective effect concentrations are an EC<sub>39</sub>, EC<sub>63</sub>, EC<sub>86</sub>, EC<sub>86</sub>, and EC<sub>98</sub>. Using gross biomass can result in particularly misleading ECs when growth rates are modest; for example, when control growth is

<sup>&</sup>lt;sup>3</sup> The specific growth rate (SGR) =dB(t)/dt/B(t), where B is biomass and t is time. If SGR is constant with time, the growth rate is exponential, and B(t)=B(0)·e<sup>SGR.t</sup>. SGR is thus the fractional rate of change of biomass with time and has units of inverse time. However, if SGR is 1/day, this does not mean that the biomass will double in one day; rather the "compounding interest" of exponential growth will mean that biomass actually increases to 2.7 times the initial value – only over short periods will growth closely adhere to this fraction (e.g., 1% growth over 0.01 day).

just a doubling of biomass over the duration in question, an  $EC_{50}$  for gross biomass actually represents no growth. Therefore,  $EC_{50}$ s reported for gross biomass, net growth, and SGR will differ from each other, and these differences will vary with exposure duration and the control SGR. Compendia that simply transcribe reported  $EC_{50}$ s can be describing a wide range of different effects.

Other factors make the meaning of reported plant ECs even less certain. As an algal suspension grows, the growth rate will decline because of nutrient depletion and self-shading. This departure from exponential growth will be most pronounced in the treatments with the highest growth rates (i.e., the control and low toxicant concentrations with little or no effect), which can allow the treatments with greater toxic effects to "catch-up" as exposure duration increases, causing ECs to increase with time. Therefore, the toxicity test actually includes a stressor (nutrient/light limitations) in addition to the toxicant that disproportionately affects the control, confounding the effects of the toxicant. In fact, some standard plant test protocols were designed to assess nutrient limitations, and the durations were selected to result in nutrient depletion (e.g., Miller et al, 1978). When used for toxicants, this type of study design can result in complicated growth dynamics and relationships that are difficult to understand and apply. Increasing values for ECs with time are evident in some published toxicity test datasets, but the opposite can be true as well, indicating additional complexities (e.g., Hoberg 1991, 1993a, b; Schafer 1994, Tang et al. 1997).

Changes in cell condition other than light and nutrient limitations might also affect ECs and their dependence on test duration. For example, chlorophyll content per cell can increase with time to compensate for reduced photosynthesis. Such changes in the chlorophyll content per cell make the use of chlorophyll as a surrogate for plant biomass problematic, possibly misrepresenting toxic effects on biomass (e.g., Boger and Schlue 1976, van der Heever and Grobbelaair 1996, Tang et al. 1997). Similarly, alterations of cell volume and density can create differences among ECs based on cell count, cell volume, cell weight, and optical density.

ECs based on oxygen production and carbon fixation can also pose interpretation problems, even if these are accepted as being proportional to net biomass production. For these measurements, short-term values for a known mass of algae are analogous to the SGR, whereas measurements long enough for substantial growth to occur would be analogous to net cumulative growth, creating differences in the meaning of ECs similar to that for net growth versus SGR. In one study (Larsen et al. 1986), the situation was especially confounded because carbon-14 fixation period was measured only at the end of a 24-hr atrazine exposure, so that the measured fixation rate reflected **both** effects of the toxicant on the rate of carbon fixation per cell and the cumulative differences in cell density due to the preceding exposure.

Macrophyte tests can be less susceptible to the issues of exponential growth and limiting conditions discussed above. Duckweed tests generally show exponential

growth, but do not often reach biomass levels sufficient to suppress growth rates. Other macrophytes have relatively modest and more linear growth during the tests. However, the issues raised above for microalgae should still be considered in the interpretation of macrophyte tests and the definition of their ECs. In addition, many macrophyte tests involve cuttings or rhizomes, which contain resources to support growth that might obscure toxic effects, especially early in tests.

The importance of these differences in the meaning of ECs is that toxicity inputs to models such as  $CASM_{ATZ}$  (Section IV.C) need to have a clear meaning that can be appropriately applied to bioenergetics equations. Likewise, the toxicity inputs to the alternative model to CASM discussed in Section IV.D need to be comparable to each other and suitable for aggregate daily effects calculations. Therefore, there is a need for the EC $_{50}$ s used in this methodology to have an appropriate "common currency". Because this methodology also needs to address effect levels other than 50%, there is also a need for consistent information on the slopes and shapes of concentration/effect relationships.

To this end, available single-species toxicity tests with atrazine were critically reviewed for information regarding exposure conditions and effects by the Great Lakes Environmental Center under support from US EPA Office of Water/ Office of Science and Technology (OW/OST). The results of this review, and of additional review of selected papers, were analyzed by US EPA to compile EC50s for SGRs and slopes for SGR versus log concentration. The SGR was selected as the "common currency" because it reduces the dependence of ECs on test duration and is most directly relevant to the candidate MEIs discussed in Sections IV.C and IV.D. These SGRs are either as reported by original authors, calculated from reported data, or estimated based on EC50s for other endpoints (see Appendix IV-1). Concentration/effect relationships were estimated using least-squares nonlinear regression as described in Appendix IV-1. The results of this review are reported in Table IV-1 and the EC50s are also plotted in Figure IV-5 as a cumulative distribution showing the mean and range of EC50s for each genus, coded to distinguish major taxonomic groups.

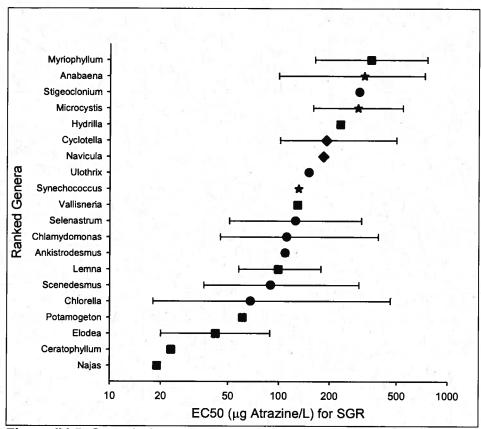


Figure IV-5 Cumulative plot of EC<sub>50</sub>s for plant growth rates, by plant genus. Symbols denote geometric means of EC<sub>50</sub>s of individual tests within genus; error bars denote range of individual EC50s. Squares denote vascular plants, circles denote green algae, diamonds denote diatoms, stars denote blue-green algae.

An analysis of variance of the individual EC<sub>50</sub> observations ( $log_{10}$ -transformed) showed an overall mean and standard deviation of 2.09 (untransformed =123  $\mu$ g/L) and 0.38. Statistically significant differences among major taxonomic groups were found, with the means being 1.95, 2.02, 2.28, and 2.45 (untransformed values 89, 105, 190, and 245  $\mu$ g/L) for green algae, diatoms, blue-green algae and vascular plants, respectively, and the pooled within-group standard deviation being 0.35. The  $log_{10}$ -transformed slopes had an overall mean of -0.05 (untransformed 0.90) and a standard deviation of 0.15. These distribution characterizations will be used in methodology evaluations in Sections IV-C and IV-D to generate estimated EC<sub>50</sub>s and slopes for plant species within these taxonomic groups.

Table IV-1 Atrazine plant toxicity tests used in assessment methodologies

	P 10711011	,	4000001114	in monous
Genus	SGR EC50 (µg/L)	Slope	Control SGR (d¹)	Reference
		GREEN AL	GAE	
Ankistrodesmus	105	1.50	0.33	Burrell et al. 1985
Alikisuodesillus	99-129	NA <sup>1</sup>	NA	Larsen et al. 1986
Chlamydomonas	390	0.68	NA	Kallqvist and Romstad 1994

Genus	SGR EC50 (µg/L)	Slope	Control SGR (d <sup>1</sup> )	Reference
	175	0.69	1.06	Schafer et al. 1993
	56-73	NA	NA	Larsen et al. 1986
	45	NA	NA NA	Hersh and Crumpton 1989
7	18	1.07	0.69	Faust et al. 1993
	26-31	NA	NA NA	Hersh and Crumpton 1989
Chlorella	91	0.52	0.26	Burrell et al. 1985
	460-600	NA	NA NA	Larsen et al. 1986
	72-94	NA	NA	Larsen et al. 1986
	55	NA	NA	Kirby and Sheahan 1994
Scenedesmus	300	NA	NA NA	Stratton 1984
00077000077700	119	1.11	NA NA	Geyer et al. 1985
	34-38	0.74	NA	Zagorc-Koncan 1996
	157	0.75	1.60	Mayer et al. 1998
	51	1.62	1.25	Caux et al. 1996
	100	1.18	NA	Versteeg 1990
	150	1.08	1.42-1.75	Hoberg 1991
	97-118	NA	NA	Turbak et al. 1986
	173	1.08	1.65	Roberts et al. 1990
Selenastrum	125	1.11	1.03	
o o i o i i a o i a i i i	115	1.01	1.35-1.60	Gala and Giesy 1990
	110-205	0.79	NA	Hoberg 1993
	a transfer			Kallqvist and Romstad 1994 van der Heever and
	310	1.18	NA	Grobbelaar 1996
	114	1.40	0.97-1.10	Parrish 1978
	72-84	NA	NA NA	Larsen et al. 1986
Stigeoclonium	264-345	NA	NA NA	Larsen et al. 1986
Ulothrix	132-172	NA NA	NA	Larsen et al. 1986
CIGUIIIX	102 112	CRYPTOMO		Laisen et al. 1900
Cryptomonas	508	NA NA	NA NA	Kallqvist and Romstad 1994
Oryptomonas		BLUE-GREEN		Tranquist and Itomistad 199-
	100-500	JEUE-GREEN	ALGAL	Stratton 1984
Anabaena	734	0.57	NA	Hughes et al. 1988
Allabacila	298-332	14	NA NA	Larsen et al. 1986
	160	1.35	0.35-0.55	Parrish 1978
Microcystis	546	0.70	NA	
Synechococcus	131	0.70		Kallqvist and Romstad 1994
Syriculococcus	131	DIATON	NA NA	Kallqvist and Romstad 1994
	471	1.29		Kallaviot and Danieted 400
Cyclotella	102-225		NA NA	Kallqvist and Romstad 1994
Cyclolella		0.72-1.03	NA NA	Millie and Hersh 1987
Navicula	500 184	NA 0.05	NA 0.96 1.03	Stratton 1984
ivavicuia	104	0.95	0.86-1.03	Hughes et al. 1988
Caratanhullium	22	MACROPH		Fabruary 4 4 4000
Ceratophyllum	23	0.72	0.04	Fairchild et al. 1998
Elodeas	89	0.73	0.07	Forney and Davis 1981
	20	0.69	0.02	Fairchild et al. 1998
Hydrilla	232	0.99	NA NA	Hinman 1989

Genus	SGR EC50 (µg/L)	Slope	Control SGR (d <sup>1</sup> )	Reference
	189	1.27	0.24	Hoberg 1991
	95	1.41	0.25	Hoberg 1993a
Lemna	58	0.88	0.23	Hoberg 1991
Lemma	148	0.61	0.21	Fairchild et al. 1998
	60	NA	NA	Kirby and Sheehan 1994
	88-94	1.00-1.14	0.40-0.44	Desjardin 2003
	164	1.05	0.02	Fairchild et al. 1998
Myriophyllum	760	1.07	0.08	Forney and Davis 1981
Najas sp.	19	0.54	NA	Fairchild et al. 1998
Potamogeton	61	0.73	NA	Forney and Davis 1981
Vallisneria	129	0.42	NA	Forney and Davis 1981

<sup>1</sup> NA=not available

## C. Methodology Evaluation Using CASM-Based MEIs

For the December 2007 SAP review, evaluations were presented in which a version of the community simulation model CASM formulated for atrazine effects assessments (CASMATZ1) was used to provide the MEI. The SAP made a variety of recommendations regarding the use of CASM, including further model development of CASMATZ1 to provide more realistic simulations of the freshwater systems of interest, validation of model-predicted atrazine effects relative to the cosm studies. and more extensive sensitivity/uncertainty analyses that considers more factors and levels, reflects natural ranges of these factors, and addresses interactions among the factors (FIFRA SAP, 2008). This subsection presents model modifications and new analyses conducted in response to the SAP's recommendations. A brief overview is first given of CASM and its formulation for atrazine risk assessment, including an updated version (CASMATZ2). Incorporation of toxicity information into CASM is then discussed, including changes made based on the review of atrazine toxicity data discussed in Section IV.B. Updates are then provided for CASM-based MEI selection and for sensitivity analyses for toxicity parameter selection and physicochemical variable inputs to the model. Finally, the utility of a CASM-based MEI for the desired assessments is discussed in light of observed sensitivities.

# 1. General Model Formulation and Parameterization, Reference Simulations

Concerns about how community processes influence manifestation of toxic effects at the population- and community-level motivated the use of cosm data as the basis for LOCs. It was thus reasonable to consider how community processes might affect extrapolation of these effects among exposure timeseries. As such, consideration was given to the use of a community simulation model as the basis for the desired MEI. CASM was selected because it has well-established applications in aquatic risk assessments and could be readily

adapted and tested for use in the atrazine assessment methodology, although similar models (e.g. AQUATOX) would also have been suitable. General information regarding CASM and its application to environmental assessments can be found in DeAngelis et al., (1989), Bartell et al. (1999, 2000), and Bartell (2003), and its specific adaptation for atrazine is described in Volz et al. (2007).

The state variables for CASM are (a) the biomasses for various species defining a simplified aquatic community and (b) concentrations for dissolved oxygen, dissolved and particulate organic matter, and certain nutrients. The state equation for each biological species is a bioenergetics equation that includes terms, as appropriate to each species, which define gains/losses of biomass from photosynthesis, respiration, food consumption, export/import, mortality, etc. For example, for phytoplankton species *i*, the basic bioenergetics equation is:

$$\frac{dB_i}{dt} = p_i - r_i - s_i - m_i - g_{ij}$$

where  $B_i$  is the biomass of the species, t is time,  $p_i$  is the gross photosynthesis rate,  $r_i$  is the respiration rate,  $s_i$  is a sinking rate,  $m_i$  is a natural mortality rate, and  $g_{ij}$  is the grazing rate by a consumer species j. Each of these rates requires specification of (a) a functional form that relates the rate to various state and input variables and (b) one to several parameters required by the function. For example,  $p_i$  is a function of light, temperature, and nutrients which includes parameters for maximum photosynthesis rate, light saturation, optimal temperature, and nutrient half-saturation concentrations (DeAngelis et al. 1989; Bartell et al. 1999, 2000; Bartell 2003). Input variables to CASM include light, temperature, nutrient imports, water flow, and depth.

For atrazine assessment needs, CASM<sub>ATZ1</sub> was formulated and parameterized to represent a second- to third-order midwestern U.S. stream that would be a typical recipient of runoff from atrazine corn and sorghum applications (Volz et al. 2007). This model aquatic community included ten species of phytoplankton, ten species of periphyton, six species of macrophytes, two species of zooplankton, five species of benthic invertebrates, seven species of fish, and bacteria in both the water column and sediment. Physicochemical environmental input variables were based on data for Upper Honey Creek (Ohio, USA), and parameters for the bioenergetics equations were obtained from peer-reviewed technical literature (Volz et al. 2007). Based on recommendations of the December 2007 SAP panel, CASM<sub>ATZ1</sub> was subject to a series of modifications by Dr. Steven Bartell (E2 Consulting Engineers, Maryville, TN, USA) under support from Syngenta and with direction from US EPA. CASM<sub>ATZ2</sub> is the October 2008 version (designated CASM\_KRNL\_GSBeta by Dr. Bartell) that incorporates the following changes:

(1) Modifications to bioenergetics equations and parameters to provide more realistic seasonal plant population dynamics (Figure IV-6).

- (2) A new default set for environmental variables that reflect average conditions over several years for Upper Honey Creek rather than a single year.
- (3) Replacement of phytoplankton species with more periphyton species (due to phytoplankton being a minor component of the systems being simulated and due to conceptual/programming difficulties in modeling a water column species that is rapidly exported downstream).
- (4) Changes to algorithms for incorporating toxicity test information into bioenergetics equations to use data on SGR rather than net growth (this provides a more direct relationship of CASM-calculated growth reductions to toxicity tests).
- (5) Provision for fixing nutrient levels at input values, rather than modeling their dynamics (because of concerns about modeling nutrient dynamics given rapid water export and about whether nutrient values input to CASM should already be interpreted as the result of nutrient processing).
- (6) Reduction of program code to a kernel that only provides the basic model simulation and outputs, which can be used by EPA-written code that provides all input control and post-processing.

Some of this CASM development was to provide more realistic plant community dynamics representative of a  $2^{nd}$  to  $3^{rd}$ -order midwestern stream. For CASM<sub>ATZ2</sub>, default reference simulations (no toxic effects with default parameter and environmental variable inputs) are shown in Figure IV-6. These show more realistic and dynamic time-progressions than did CASM<sub>ATZ1</sub>. Both options for nutrient handling are shown; the higher nutrient levels that result from fixing these values result in higher production and some shifts in relative importance of different plant taxa.

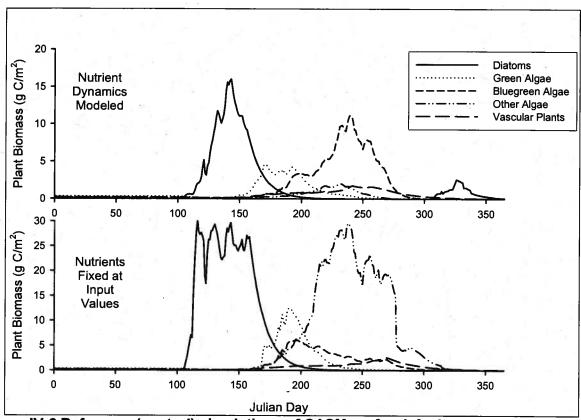


Figure IV-6 Reference (control) simulations of CASM<sub>ATZ2</sub> for default parameters and input variables, run with simulation of nutrient dynamics (top panel) and with nutrients fixed to input values (bottom panel)

## 2. Incorporation of Toxicity Information into Model

One challenge in applying a bioenergetics-based community model such as CASM to toxicity assessments is that toxicity tests do not directly address the effects of the chemical on the specific parameters of the bioenergetics state equation (e.g., Equation 1). For example, a plant growth test provides information on the net growth rate, but not on how specific aspects of photosynthesis and respiration functions are being affected. Even for well documented tests, there is insufficient information to directly assess all the model parameters.

To address this problem, CASM uses inputted relationships for toxic effects versus atrazine concentration to estimate a single "toxic effects factor" (TEF)<sup>4</sup> for

<sup>&</sup>lt;sup>4</sup> To do this, CASM uses the bioenergetics equation for a species to simulate growth under toxicity test conditions for each exposure concentration of interest, adjusting the TEF to cause the model-predicted growth effect at an exposure concentration to match the effect in the concentration/effects relationship designated for the species. Because toxicity tests generally have conditions favorable to the test organisms, plant TEFs are computed assuming optimal conditions of nutrition, temperature, light, etc. One consequence of a TEF based on optimal conditions is that, when this TEF is used for suboptimal conditions in model simulations, the level of effect can differ from that in the toxicity test. Using the ECs

each concentration that, when used to adjust selected model parameters, will reproduce the observed degree of toxic effect at that concentration (DeAngelis et al. 1989; Bartell et al. 1999, 2000; Bartell 2003; Volz et al. 2007). For plants, CASM<sub>ATZ</sub> (CASM<sub>ATZ</sub> refers collectively to CASM<sub>ATZ1</sub> and CASM<sub>ATZ2</sub>) offers two alternatives for how model parameters are altered by the TEF. For the "General Stress Syndrome" (GSS), the TEF is used to (a) reduce photosynthesis by decreasing the maximum photosynthesis and increasing light and nutrient saturation parameters and (b) increase the various loss terms, such as respiration, in the bioenergetics equation. For the "Photosynthesis Stress Syndrome" (PSS), only the maximum photosynthesis parameter is modified, more in keeping with atrazine's mechanism of action on photosynthesis. The analyses presented in this report exclusively use the PSS; unreported results show the GSS to produce very similar risk factors.

CASM<sub>ATZ</sub> also offers different options for the shape of the effects/concentration relationship, including the sigmoidal relationship described in Section IV.B for the analysis of the toxicity data. This relationship is used exclusively for the analyses in this report. Other options in CASM<sub>ATZ</sub> include linear and probit relationships; unreported results show that these other options produce risk factors very similar to the option selected.

For evaluations reported in the December 2007 SAP review, a default  $EC_{50}$  was assigned to each  $CASM_{ATZ1}$  species based on observed  $EC_{50}$ s for similar species (Volz et al. 2007). The sensitivity of risk assessments to these default selections was evaluated by randomly selecting alternative  $EC_{50}$ s from the overall distribution of toxicity test results. Based on the reevaluation of the toxicity data (Section IV.B), it was decided that only such random selection of the  $EC_{50}$  (and effects/concentration slope) should be done because of uncertainties about assigning default values to species. Therefore, sets of  $EC_{50}$ s and slopes were assigned randomly to each species from the distributions specified in Section IV.B. Fifty such sets were developed for use in all analyses provided in Sections IV.C.3 to IV.C.5.

Toxicity values were also assigned to the animal species. Because the lowest  $EC_{50}$  for any animal species was much greater than the  $EC_{50}$ s for most of the plant species, these toxicity values were simply set high enough to avoid any response even at the highest concentration, rather than making specific assignments from the toxicity literature. Thus, assessment results are not sensitive to the animal toxicity value selection, which is not evaluated as part of this report.

for the SGR simplifies calculations and reduces uncertainties that might arise if CASM uses a different control growth rate from that in the toxicity test.

#### 3. Model Effects Index Selection

The basic output of CASM is a time-series of daily biomass values for each modeled species over a calendar year. Various possibilities exist for synthesizing this information into an MEI for the primary producer community. The MEI might address how total plant biomass or production is perturbed in an exposed system compared to an unexposed system, or might also address perturbations in the relative biomasses of each species. The MEI might indicate the maximum perturbation across the entire simulation, the average perturbation over the entire simulation, an average perturbation during a fixed time window during the simulation, or a maximum running average of the perturbations.

Two measures were considered for use in the MEI. One was simply the ratio of daily values for total plant biomass (TPB), summed over all plant species, for a simulation with atrazine exposure to that in a simulation without exposure. The other variable was the Steinhaus Similarity Index (SSI). The SSI quantifies the similarity between two communities (in this case, exposed and unexposed model-calculated communities). For each day of the simulation, the SSI is calculated as:

$$SSI = 2 \cdot \frac{\sum_{i=1}^{n} min(B_{R,i}, B_{E,i})}{\sum_{i=1}^{n} B_{R,i} + \sum_{i=1}^{n} B_{E,i}}$$

where  $B_{R,i}$  is the daily biomass of the i<sup>th</sup> species in the reference (control) simulation and  $B_{E,i}$  is the daily biomass of the i<sup>th</sup> species in the atrazine-exposed simulation. SSI values thus reflect changes in relative population sizes, ranging from 1.0 for identical community structures to 0.0 for completely disjoint communities. This type of measure was included to address relative species abundances in the assessment, rather than just total primary productivity.

For the MEI to reflect adverse effects, the TPB ratio and SSI are first subtracted from 1.0 and then multiplied by 100 to represent percent deviations (TPBD, SSID) from the control. These deviations then need to be averaged over an assessment period as discussed in Section IV.A.2. Options of 7, 14, 30, 60, and 120 days for the assessment period were considered. Longer periods (such as the 365-day period in the December 2007 SAP) were not considered because they are longer than needed to bracket periods with significant atrazine exposures and would often contain extended periods of no effect that result in misleadingly low MEIs. Thus, ten MEI options were considered: five assessment periods, each with a TPB-based and a SSI-based MEI.

Selection from among the possible MEIs was based on the following evaluations, following the general methodological strategy outlined in Figure IV-3 and Figure IV-4.

- (1) 50 sets of toxicity parameters were generated, each set consisting of an EC<sub>50</sub> and slope for each plant species, randomly selected from the distributions identified in Section IV.B.
- (2) Model simulations were conducted for no atrazine exposure and for each cosm exposure/toxicity parameter set combination (78x50), with atrazine exposure starting on Julian day 105. All these runs were conducted with CASM<sub>ATZ2</sub> using default input variables and parameters. The computational time step was 0.1 day, the nutrient cycling calculations were enabled, and other model options (PSS, concentration/effects relationship shape) were as already specified.
- (3) For each cosm treatment/toxicity parameter set combination (78x50), the computed daily plant biomasses were used to compute daily values for (a) SSID, the percent reduction of the SSI from its maximum value of 1.0, and (b) TPBD, the percent reduction in TPB from that in the reference simulation. These daily values were used to compute maximum running averages for each assessment period of interest, to provide MEI values for each MEI option.
- (4) An LOC<sub>MEI</sub> for each MEI option/toxicity parameter set combination (10x50) was computed by correlating Brock scores to their respective MEIs and finding the value of the MEI that equalized false positives and false negatives (e.g., Figure IV-3).
- (5) For constant exposures of 3, 7, 14, 30, 60, 120, and 260 days (starting at Julian day 105) and for each MEI candidate/toxicity parameter set combination (10x50),  $CASM_{ATZ2}$  simulations were iteratively run to determine the concentration that results in an MEI equal to the  $LOC_{MEI}$ .
- (6) For each example chemograph in Figure 3-2 and for each MEI candidate/toxicity parameter set combination (10x50), CASM<sub>ATZ2</sub> simulations were iteratively run to determine the risk factor (multiplicative factor by which chemograph concentrations must be reduced so that the MEI equals the  $LOC_{MEI}$ ).

Figure IV-7 compares results for all SSI-based MEI options and one TPB-based option, using median results across the 50 toxicity parameter sets (other TPB-based options show similar trends). The left panel shows constant exposure concentrations equivalent to the LOC<sub>MEI</sub> for various exposure durations. The lines for the various MEI options are indistinguishable, except at short durations for the TPB-based MEI. These lines are plotted with the cosm data to illustrate the discrimination of the cosm score groups and the time-dependency imposed on this data by CASM; however, it should be noted that the data points sometimes reflect highly variable exposures, so any comparison to the lines is approximate. The right panel shows the risk factors computed for the various example chemographs (Figure IV-2). For each chemograph, the ratio of the

largest to smallest risk factor among the different MEIs is small, ranging from 1.04 to 1.55 among the chemographs. Thus, results are very insensitive to the choice of the MEI. The 30-day average SSI deviation is used as the MEI in other analyses discussed in this section because its risk factors are always intermediate to the risk factors for other options, usually being with 10% and always within 30% of these other factors.

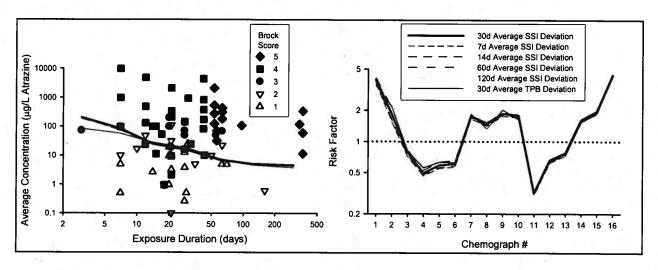


Figure IV-7 Effect of CASM-based MEI selection on estimated LOCs for constant exposures (left panel) and risk factors for example chemographs (right panel)

# 4. Sensitivity of Results to Toxicity Parameter Selection

The MEI selection in the previous subsection was based on median results of simulations conducted with 50 different toxicity parameter sets. Figure IV-8 shows the variability of risk factors across these different toxicity parameter sets when the MEI is the maximum 30-day running average SSI deviation (note that the scale of this figure includes 20-fold deviations from 1.0 in contrast to the 5-fold deviations in Figure IV-7).

This analysis demonstrates great sensitivity of a CASM-based assessment to the selection of the toxicity parameters. Risk factors vary by 5-fold to 100-fold depending on the nature of the chemograph (Figure IV-8). For almost all these chemographs, the range of risk factors extends from above to below 1.0 as a function of the toxicity parameter selection, and the degree to which exposures must be reduced to equal the LOC<sub>MEI</sub> is highly uncertain.

This sensitivity can be attributed to the limited number of plant species that dominate the model plant community at any one time. Although CASM<sub>ATZ2</sub> has a large number of plant species for a community simulation model, the community can be dominated by one or a few species at any given time. Therefore, community dynamics can be very sensitive to the toxicity parameters selected for individual species. This sensitivity exists not only for the absolute values of the community dynamics, but also for the relative extrapolations across exposure

time-series represented by the risk factors. Even if toxicity parameter selection was further refined for particular species, large uncertainties in risk factors would persist given the variability of toxicity values within a species (Figure IV-5).

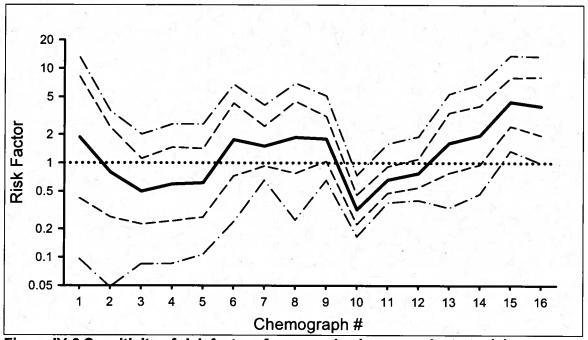


Figure IV-8 Sensitivity of risk factors for example chemographs to toxicity parameter selection.

Simulations were for default environmental conditions, a Julian day 105 start for cosm exposures, and the model effects index set to the maximum 30-day average SSI deviation. The solid line denotes average results, the dashed lines plus/minus one standard deviation, and the dash-dotted lines the minima and maxima (n=50).

This large sensitivity of risk factors to toxicity parameter selection requires careful consideration for positioning a risk threshold within this uncertainty range. This does not necessarily require selecting a high percentile in the ranges shown in Figure IV-8. Because the basic level of protection is determined by how LOC<sub>MEI</sub>s are set relative to cosm data and because the high percentiles in Figure IV-8 reflect unlikely combinations of toxicity parameters, an argument might be made for using a moderate percentile. In any event, identification of a risk threshold would entail difficult and complex considerations, and represents a disadvantage of CASM-based MEIs.

# 5. Sensitivity of Model Results to Environmental Parameters

In addition to the selection of toxicity parameters, any implementation of CASM entails specification of many other input variables and parameters, especially the various environmental input variables (light, temperature, nutrients, depths, flows) and the bioenergetics parameters and community structure. Furthermore, for the simulations of the cosm exposures (Figure IV-3), there is a need to select a starting date for these exposures within the simulation that is appropriate for

the community dynamics (Figure IV-6). As already noted, an *a priori* requirement for the MEI is that it be generic. Otherwise, the MEI would need to be tailored to each cosm and field-site of interest, which not only would be extremely difficult, but also very uncertain because of the lack of empirical evidence to confirm model predictions regarding effects of site attributes. Thus, it was desired that CASM-based risk factors not be sensitive to a reasonable range of the input variables and parameters. Although absolute plant community dynamics might be sensitive to such changes, it is important that the relative extrapolations among different exposures (i.e., the risk factors) are not sensitive.

The sensitivities of the risk factors to the cosm exposure start date and to various environmental factors (light, temperature, nutrients, depth, flow) were evaluated. For the start date, the default date of 105 days was changed to 20 days earlier and 30 days later in 10 day increments. For each environmental factor, the Agency examined sensitivity to four changes to the default inputs for CASMATZ2. Two changes involved decreasing and increasing the environmental variable on each day by a fixed factor. For temperature, this factor was 1.2, which produced a range in the maximum summer temperature of 20-30 C, not unreasonable for the range of streams in the Midwest corn-growing areas of interest. For the other variables, this factor was 2.0, which is rather modest given the range of stream sizes, flows, nutrients inputs, shading, etc. possible among these streams. Another attribute of interest regarding the environmental variables was the daily and seasonal variability. The third change for this sensitivity analysis was to smooth out this variability using a 180-day running average of the default values while the fourth change increased the variability by doubling the difference between the smoothed and default time-series. It should be noted that these specific changes were made to establish whether substantial sensitivity was present, not to define uncertainties associated with actual distributions of these variables.

Figure IV-9 provides the results of the sensitivity analyses for exposure start date and for environmental variables. For all the variables, risk factors varied by a factor of 2 or more for at least some of the example chemographs, and in some cases the variation was a factor of 5-10. Although less extreme than the sensitivity to toxicity parameter selection, this sensitivity to the site attributes is substantial and would need to be accounted for in uncertainty analyses if a CASM-based MEI is used in the desired generic methodology.

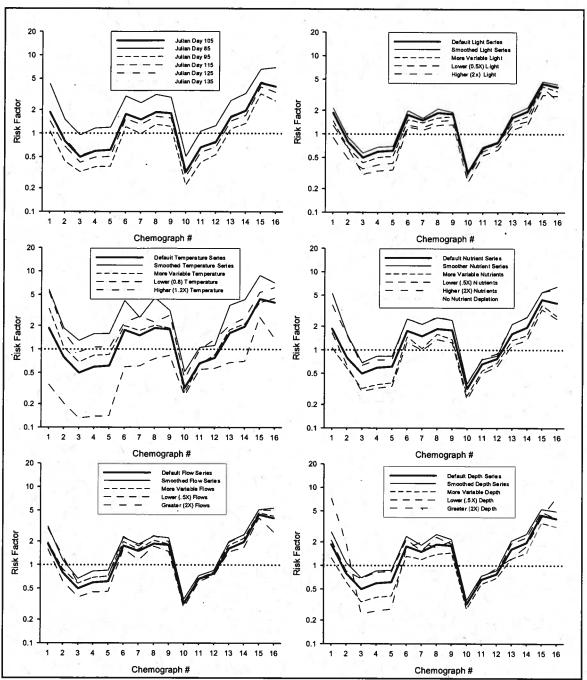


Figure IV-9 Sensitivity of risk factors for example chemographs to start date for cosm simulations and to various environmental parameters.

Each line is median of results from 50 sets of toxicity parameters. All input variables and

parameters at default values except for the change indicated in the legends for the line.

The results in Figure IV-9 also serve to illustrate some of the complexities that might need consideration for further evaluations of the uncertainties associated with the values assigned to these and other parameters (whether for generic or site-specific applications). For example, the reduced temperature option in the sensitivity analysis showed especially large impacts on the risk factors,

decreasing them by as much as 5-fold from the default case. A likely explanation for this is that lower temperature delayed the initial period of major plant growth (Figure IV-5) beyond the Julian day 105 start for the cosm exposure simulations. Depending on the start date for significant exposures in the example chemographs, the effect of temperature would have different impacts on model-predicted effects and thus affect the extrapolation of effects from the cosm data to the field exposures. This creates the need to consider various correlations in the data. For a lower temperature, should the cosm exposure simulations have later start date, so that LOC<sub>MEI</sub>s are more representative of the lower range of temperature that occurs in natural systems? Should simulations at lower temperatures also have different bioenergetics for the plant community, more indicative of communities adapted to lower temperatures? This issue is just one of many that would need to be considered in development of CASM-based methods to address sensitivity to site attributes.

# D. Methodology Evaluation Using MEIs Based Directly on Plant Toxicity Sensitivity Distributions

### 1. Formulation of the Plant Assemblage Toxicity Index

This section presents an alternative to CASM-based MEIs based directly on the same plant toxicity sensitivity distributions used for CASM toxicity parameters. As already discussed, the MEI simply needs to provide a measure of cumulative toxic impact of a series of daily exposures that provides a reasonable basis for comparing the relative impacts of different exposure time series. A simple way to do this is to use laboratory toxicity test results to compute the aggregate effect of any daily concentration on the average growth rate of an assemblage of plant species. Figure IV-10 illustrates such a calculation. For simplicity, the left panel of the figure characterizes the plant assemblage based on a single species sensitivity distribution of plant growth EC<sub>50</sub>s; however, this is easily extended to multiple distributions for both EC<sub>50</sub>s and slopes. This distribution provides the needed information for percent growth inhibition versus concentration relationships for the assemblage of species, three of which are represented in the middle panels of Figure IV-10. For actual analyses using this methodology. toxicity parameters are randomly selected from the sensitivity distributions to compute 1000 such curves. This selection is not intended to represent actual species, but rather is a mathematical approach for conducting desired integrations over the various sensitivity distributions. The individual curves for the entire assemblage are averaged to provide an inhibition versus concentration curve for the assemblage (right panel of Figure IV-10), the "Plant Assemblage Toxicity Index" (PATI). This index can be computed for each day's concentration and provides an analog to the daily SSIDs or TPBDs from CASMATZ; therefore this index fits into the general assessment strategy illustrated in Figure IV-3 and Figure IV-4. Like the SSID or TPBD, the daily PATI values are averaged over an assessment period to provide the MEI.

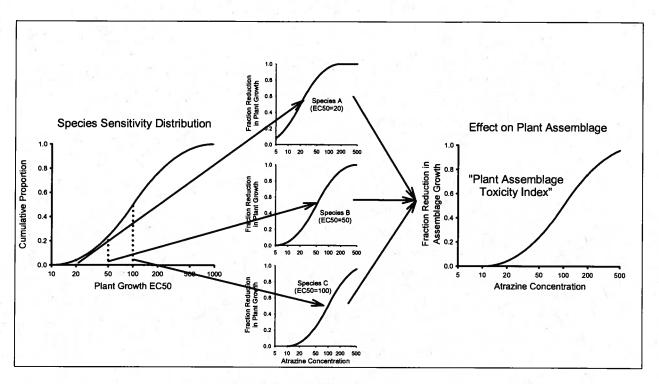


Figure IV-10 Conceptual Model for Plant Assemblage Toxicity Index

This new index can also be viewed as a subcomponent of the CASM-based indices. Risk factors from the CASM-based methodology reflect the effect of atrazine on the various processes incorporated into CASM<sub>ATZ</sub>. The driving force is atrazine-induced reductions in the daily growth rates for each plant species in the model. These growth rate reductions alter absolute and relative biomasses, which in turn influence further biomass changes, both directly and indirectly by alterations in competition, grazing, etc. This raises the question of what processes most influence extrapolations among time-series. In particular, how important is the original driving force of growth rate reductions compared to other model processes that determine how such reductions affect future plant biomasses? In other words, how much added value is provided from modeling these other processes beyond that from the growth rate reductions caused by atrazine?

This question could have been addressed using CASM by basing the MEI only on the average reduction in plant growth rates, weighted by the relative species biomass in the reference simulation. Such an index would be specific to the CASM configuration used, but without consideration of how toxicity is manifested into perturbed biomasses by various community processes. However, because CASM is run over many variations of the toxicity values for each species, median results over these simulations would reflect an integration for each species over the species sensitivity distributions used to parameterize CASM, and thus be similar to the PATI-based methodology.

#### 2. Model Effects Index Selection

Similar to the CASM-based methodology, this alternative approach requires selection of an assessment period over which the PATI is averaged. For CASM, the assessment period can be less than typical cosm exposure durations, because cumulative effects on community dynamics are estimated; therefore, shorter averaging periods for effects can be reflective of the entire period for exposure. However, for the PATI, the effects addressed are restricted to the actual period of exposure. Thus, the assessment period should be longer than most of the cosm studies used to determine the LOC<sub>MEI</sub>. Otherwise, the implication is that any cosm exposure longer than the assessment period is of no consequence to effects.

To evaluate consequences of the assessment period choice, assessment periods of 10, 30, 90, 180, and 270 days were evaluated. The two shorter periods were included only to demonstrate consequences when the periods are arguably too short relative to the typical cosm exposure. The left panel of Figure IV-11 shows the LOC concentrations for constant exposures and the segregation of the cosm Brock score groups by this method. Again, this comparison of LOC concentrations for constant exposures to the average concentrations for the cosms is only approximate, because many of the cosms have exposures which are not constant. However, these LOCs for constant exposure provide a useful indication of the type of time-dependence that the model is imposing on the cosm data, which is very similar to the CASM-based MEI.

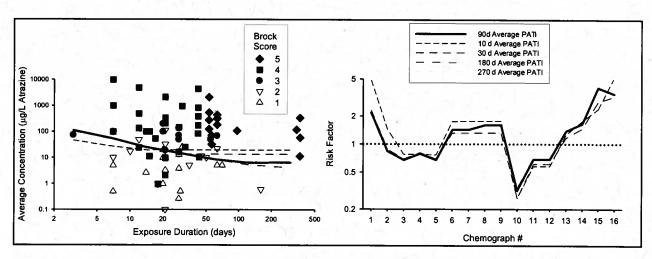


Figure IV-11 Effect of PATI-based MEI selection on estimated LOCs for constant exposures (left panel) and risk factors for example chemographs (right panel)

The lines on Figure IV-11 also illustrate a mathematical property of this MEI – that LOC concentrations increase for constant exposures less than the assessment period and become constant at exposures longer than the assessment period. The lines intersect near 30 days because this is near the middle of the cosm data to which these lines are calibrated. As a consequence,

all the lines except for the 10 day assessment period are superimposed for constant exposures less than 30 days. At longer durations, lines remain superimposed until the duration for each is exceeded, at which point it provides a higher LOC concentration than the lines for assessment period durations.

The right panel of Figure IV-11 shows the consequences of assessment period choice on estimated risk factors for the example chemographs. No differences exist between the longer three periods. The shortest (10-day) period does result in higher risk factors for the chemographs with the shortest exposures (#1-9 and #16) and lower risk factors for chemographs with more prolonged exposures (#10-15), but, even for this arguably too short assessment period, the differences are usually minor. The 30-day period results in even smaller differences from the longer periods, and is indistinguishable from them for about half of the chemographs.

Thus, as with CASM, results are not sensitive to the choice of the MEI assessment period for the alternative PATI-based methodology. A 90-day assessment period is used for subsequent analyses in this section because it is sufficiently long relative to the cosm study durations and the duration of significant exposures in example chemographs, and because longer assessment periods produce indistinguishable risk factors.

### 3. Comparison of CASM- and PATI-Based Risk Factors

Figure IV-12 compares estimated risk factors for example chemographs using the CASM-based and PATI-based MEIs. The CASM-based risk factors are the median results for the 50 toxicity parameter sets, with environmental variables and other parameters set at default values and with the MEI set to the maximum 30-day running average SSI. The PATI-based risk factors are for the 90-day assessment period and the default EC50 and slope distributions used in CASM, with each of the four EC<sub>50</sub> distributions being equally weighted in the calculation of the PATI. Basing this comparison on the median result across toxicity parameter sets for CASM is appropriate because the PATI-based MEI integrates across the species sensitivity distribution and thus would be analogous to the median of multiple CASM applications. The risk factors are very close for the two methodologies, never differing by more than a factor of 1.4 and sometimes being indistinguishable, although this agreement would be less for some CASM-based evaluations with non-default parameters and input variables. The agreement between the two methods suggests that other processes within CASM are of lesser importance than the basic toxicity driving force. This underscores the question of whether the additional processes within CASM provide sufficient added value to justify the complexities and difficulties of implementing a CASMbased methodology.

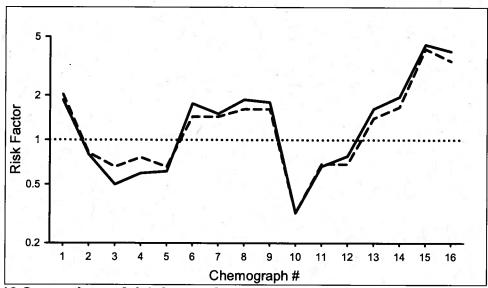


Figure IV-12 Comparison of risk factors for example chemographs for CASM-based and PATI-based MEIs.

For CASM, solid line is median results of 50 toxicity parameter sets using default conditions for input variables and parameters and the maximum 30-day running average SSI. For PATI, dashed line is for a 90-day assessment period and equal weighting of the default species sensitivity distributions used in CASM.

### 4. Sensitivity of Results to Effects Model Parameterization

Because the PATI represents an integration of the species sensitivity distributions, uncertainties of toxicity parameter selection from within these distributions are not relevant, in contrast to toxicity parameter selection for the limited number of species used in CASM. And because this alternative methodology does not attempt to address the possible effects of environmental factors, this source of uncertainty is also not relevant. However, there are two sources of parameterization and model uncertainty that do warrant consideration in sensitivity analyses for the PATI-based methodology.

First, the species sensitivity distributions are uncertain, especially regarding their representativeness of species assemblages in specific systems. To address the potential importance of this uncertainty, a sensitivity analysis was conducted using four alterations to the distributions reported in Section IV.B. Two of the alterations involved decreasing and increasing the means of the  $\log_{10} EC_{50}$  distributions by 0.3. This represents a two-fold increase or decrease in the sensitivity of the assemblage being assessed, which is a major shift nearly equal to the standard deviation of the distributions of observed  $EC_{50}$ s and several times greater than one standard error of the overall mean  $EC_{50}$ . The other two alterations involved changing the dispersion of the distributions, increasing and decreasing the observed within-taxa pooled standard deviation of 0.35 by 0.1, a change greater than the confidence limits for this parameter.

Figure IV-13 shows how risk factors changed due to these alterations of the sensitivity distributions. When the means of the EC $_{50}$  distributions are altered (left panel of Figure IV-13), risk factors changed from the values for the default case by less than a factor of 1.2, and usually less than a factor of 1.1, except for chemograph #1, for which changes were up to a factor of 2. When the dispersion of the sensitivity distributions is altered (right panel of Figure IV-13), even less impact on risk factors is observed, with risk factors changing by no more than a factor of 1.1, except for chemograph #1, for which the changes were up to a factor of 1.25. Considering the large sensitivity distribution alterations examined, these results demonstrate very little sensitivity of this method to uncertainties in the toxicity data.

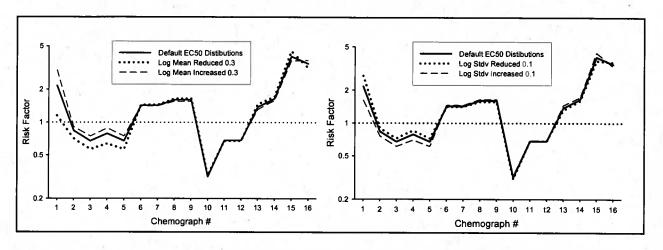


Figure IV-13 Sensitivity of risk factors for example chemographs to toxicity distributions used to compute PATI.

A noteworthy aspect of the results in Figure IV-13 is that *increasing* the toxic sensitivity of the plant assemblage (which increases the MEI for any exposure time-series) *decreases* the risk factors for the example chemographs with the shortest exposures (chemographs #1-5). Although this may seem counterintuitive and inappropriate, it reflects the fact that the MEI is not providing an absolute measure of effects, but rather is used for extrapolating among exposure time-series, based on an LOC<sub>MEI</sub> calibrated to the cosm data. The fact that higher MEIs translate into lower risk factors for these chemographs simply indicates that greater sensitivity of the assemblage increases the MEIs more for the cosm exposures than for these chemographs.

The second area of uncertainty that warrants consideration is the use of simple averaging of toxic effects across days. Such simple averaging constitutes a linear assumption about how the degree of toxic effect should be weighted, such that a 50% reduction is weighted five-times a 10% reduction (so that a 50% reduction in assemblage growth rate for 1 day is equivalent to a 10% reduction for 5 days, etc.). This might seem no different than the simple averaging of the SSID or TPBD in the CASM-based method, but these CASM indices involve the state variables of ultimate concern, while the weights given to effects on growth

rate within CASM are not necessarily linear. If the evaluations of the uncertainty of CASM-based results are expected to address how various factors affect this weighting, comparable evaluations of this alternative methodology should be made.

The sensitivity of the results to the assumption of simple averaging can be evaluated by using nonlinear weighting of the degree of effect on each day. Figure IV-14 compares linear weighting to two alternatives — a square root weighting in which lower level effects receive greater relative weight (e.g., a 50% reduction is weighted 70% relative to a 100% reduction) and a squared weighting in which lower level effects receive less relative weight reduction (e.g., a 50% reduction is weighted 25% relative to a 100% reduction). Although these functions represent rather extreme nonlinearities in the weighting, they have relatively little impact on risk factors (Figure IV-14). The changes in the risk factors from linear weighting were no greater than a factor of 1.2, except fot chemograph #1, for which the changes were up to a factor of 1.9.

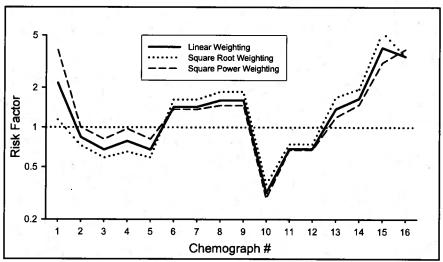


Figure IV-14 Sensitivity of risk factors for example chemographs to weighting relationship for PATI

### 5. Effect of New COSM Data Interpretation on Risk Factors

Relative to the results presented at the 2007 SAP, the risk factors presented earlier in this section reflect changes both to the effects model used (update to CASM<sub>ATZ2</sub> and the new use of the PATI) and updates to the cosm Brock scores and exposure profiles (Section III); however, the analyses presented thus far only address issues of model formulation and suitability.

Figure IV-15 illustrates how risk factors are affected due to the updates in the cosm data. The solid line denotes results based on the updated cosm data as presented in Section III. This repeats results from Sections IV.D.2-4 for the PATI-based method using the default sensitivity distributions and a 90-day assessment period (e.g., Figure IV-14). The dashed line denotes application of

this same method to the old cosm data presented at the 2007 SAP. For all the chemographs, the updated cosm data resulted in risk factors increasing by a factor of 1.5 to 2.1. The dashed-dotted line denotes results that are based only on the updated Brock scores, but not the updated exposure profiles. The small differences between the dashed and dashed-dotted lines indicates that the Brock score modifications had little effect on estimated risk; rather, incorporating more appropriate exposure profiles into the analyses was responsible for almost all the increased risk. Because these new exposure profiles account for dissipation of atrazine in the cosm studies, the observed effects in the cosm studies are being related to lower exposures. This results in a lower LOC<sub>MEI</sub>, and thus greater estimated risk for the field exposure profiles represented by the example chemographs.

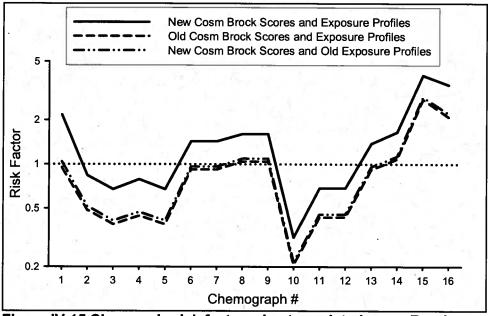


Figure IV-15 Changes in risk factors due to updated cosm Brock scores and exposure profiles. All risk factors are for the PATI-based method using default toxicity distributions and a 90-day assessment period.

# E. Comparative Suitability of CASM- and PATI-based MEIs for Atrazine Assessment Methdology

Before summarizing the relative merits of the two effects models evaluated here, a few important aspects of the atrazine assessment strategy should be emphasized. Both of these models serve the same, limited role in the general assessment strategy illustrated in Figures IV-3 and IV-4. In this strategy, the cosm data define the basic relationship of the LOC to exposure, while the effects model only provides an MEI that is informative of the relative severity of different exposure time-series shapes. The models differ only in the daily measure of effects provided to this process (e.g., the SSID versus the PATI), both of which are then averaged over a suitable assessment period. In addition, it needs to be reiterated that the model needs to be applied generically (not a function of physical/chemical/biological

attributes of either the individual cosms and natural freshwater systems to be assessed) because adequate data on system-specific attributes and their effect on risk is not available.

The evaluation of both effects models demonstrates that the PATI-based MEI for the atrazine methodology results in risk factors that are insensitive to uncertainties in its parameterization, in contrast to CASM-based MEIs. The sensitivity of risk factors to various aspects of CASM parameterization reflects CASM's demonstrated utility in site-specific applications, but creates difficulties in defining and addressing uncertainties for the desired generic application. Furthermore, the risk factors computed using the PATI-based MEI are extremely close to the median and well within the variability observed in the sensitivity analyses for the CASM-based methodology. Based on these considerations, the Agency proposes that the atrazine assessment methodology use a PATI-based MEI rather than a CASM-based MEI.

It should be recognized that the conclusions about CASM based on CASM<sub>ATZ2</sub> are different than those for CASMATZ1 presented at the December 2007 SAP review. For this earlier model, little sensitivity existed to the exposure start date and environmental variables, and only moderate sensitivity to toxicity parameter selection (US EPA, 2007). Thus, CASMATZ1 appeared to be a suitable candidate for providing the MEI for the desired generic assessment methodology, contingent on additional sensitivity analyses. However, concerns about unrealistic seasonal dynamics of plant populations in CASM<sub>ATZ1</sub> led to the development of CASM<sub>ATZ2</sub>. The more realistic and dynamic plant population changes in CASM<sub>ATZ2</sub> have apparently resulted in considerable sensitivity to selections for toxicity parameters. exposure start date, and environmental variables, making it less suitable for the desired generic atrazine assessment methodology. This not only led to consideration of alternative approaches for the MEI, but also is the reason that some of the recommendations from the December 2007 SAP regarding CASM were not pursued. The SAP recommendations included additional model validation, and expanded sensitivity/uncertainty analyses involving other parameters (e.g., bioenergetics and community relationships), realistic distributions for the various input variables and parameters, and correlations among variables. Although the sensitivity analyses reported above incorporated some of the recommended expansions, most were not pursued because such efforts would not negate the uncertainties already established and would probably expand on them.

## F. Uncertainty Assessment for Risk Factors

In previous sections, the sensitivity of risk factors to model parameterization was examined for both the CASM-based and PATI-based methodologies. For final application of either of these models, estimates of uncertainties for the risk factors due to model parameterization issues would be desired. This would be accomplished by repeated evaluations of the risk factor using random assignments of model parameters from uncertainty distributions assigned to each parameter

(Monte Carlo analyses). This requires identification of each model parameter to which risk factors are sensitive, specification of an uncertainty distribution for the parameter, and consideration of the correlations among the distributions for different parameters.

For the PATI-based methodology, the primary parameterization uncertainty is the plant toxicity sensitivity distributions upon which PATI calculations are based. For the sensitivity analyses, means of the  $log_{10}EC_{50}$  distributions were changed by  $\pm 0.3$ (a factor of two for the mean EC<sub>50</sub>) and the standard deviations of the log<sub>10</sub>EC<sub>50</sub> were changed by ±0.1. Both of these changes are substantial relative to the observed variability of individual EC<sub>50</sub> observations within and among the genera reported in Table IV-1. For example, for green algae, the overall mean EC<sub>50</sub> of 29 observations across 7 genera is about 105 µg/L. By reducing this to two-fold, the sensitivity analysis assumed that the mean was actually less than the means of all the genera and less than >80% of the individual observations. Similarly, by raising the overall mean two-fold, this was greater than the mean values for all but one genera and greater than >80% of the individual observations. There are no grounds for assuming that the sensitivity distributions of the plant assemblages in different systems might vary by more than this. Therefore, these conservative changes used in the sensitivity analyses were also adopted as 95% limits for the mean and standard deviation of the log<sub>10</sub>EC<sub>50</sub> distributions for use in the uncertainty analyses.

The uncertainty analyses for PATI-based risk factors begin with generating 500 randomly-selected parameter sets (mean, standard deviation) for the log<sub>10</sub>EC<sub>50</sub> sensitivity distributions for the four taxonomic groups specified in Section IV.B. The means of these distributions were randomly selected from a normal distribution with the default log mean for the taxonomic group (Section IV.B) and a standard deviation of 0.15 (so that ± 2 standard deviations corresponds to the ±0.3 variation in the sensitivity analysis). The standard deviations of these distributions were randomly selected from a normal distribution with a mean of 0.35 (the pooled standard deviation from Section IV.B) and a standard deviation of 0.05. On this loa scale, these means and standard deviations were assumed to be uncorrelated. Each of these 500 distributions was then separately used in the PATI-based methodology described in Section IV.D.1.to compute (a) an LOC<sub>MEI</sub> based on the cosm data and (b) a risk factor for each chemograph of interest. Thus, there is no single LOC or risk factor, but rather distributions characterized by 500 values for each parameter. Risk decisions must be based on various percentiles within the distribution of risk factors. Software to implement this analysis was written and was used for the results presented in Sections V and VI.

For the CASM-based methodology, parameters to include in an uncertainty analysis were not completely identified because sensitivity analyses conducted on just a subset of the possible parameters already indicated substantial uncertainty issues that made additional sensitivity analyses moot. For the same reason, efforts were not made to establish final parameter distributions and correlations for uncertainty analyses. As such, reasonably complete uncertainty analyses cannot be done with

the CASM-based methodology. However, in order to provide some illustration of uncertainty in the comparisons of PATI-based and CASM-based risk factors in Sections V and VI, a partial uncertainty analysis was conducted with 100 CASM-based risk factor evaluations using randomly selected sets of toxicity parameters (selected as described in Section IV.C.4), starting dates (randomly selected between Julian day 85 and 135), and environmental variable time-series (randomly selected from the ranges used in the sensitivity analyses in Section IV.C.5). It should be emphasized that this is for illustrative purposes only and, had CASM been selected as the effects model for the atrazine assessment methodology, considerably more development of this uncertainty analysis would have been necessary.

Finally, it should finally be noted that the model parameterization uncertainty discussed here is just one source of uncertainty. The basic effects model structure (in comparison to other possible models and to actual natural systems) represents an unavoidable uncertainty that cannot be quantified, although the consideration of nonlinear weighting in Section IV.D.4 and comparisons across models, such as in Section IV.D.3, do provide some information regarding model uncertainty. The cosm data on which the LOC<sub>MEI</sub>s are based are also a source of uncertainty, especially with respect to the overlap of Brock scores discussed earlier. Consequently, one major source of uncertainty for risk factors would be how false negatives and positives are balanced in setting the LOC<sub>MEI</sub>. The software developed for PATI-based analysis allows for changing this balance, and the sensitivity of risk factors to this balance will be addressed in subsequent sections.

# V. Updated Results Of The Atrazine Ecological Exposure Monitoring Program (AEEMP)

The US EPA IRED for atrazine required Syngenta to initiate the AEEMP to monitor headwater streams in the corn and sorghum growing areas of the United States. The AEEMP is a statistically designed monitoring program that allows the Agency to make inferences about levels of effect not only within the sampled watersheds but also throughout the pool of corn/sorghum watersheds from which these sites were selected (US EPA, 2007). The Agency analyzed the surface water monitoring data (i.e. chemographs) using the approaches described in Section IV to determine whether measured atrazine concentrations in the streams exceed the LOC for aquatic plant communities.

This section updates the US EPA preliminary evaluation of the AEEMP based on monitoring data collected between 2004 and 2006 and analyzed using the earlier CASM<sub>ATZ1</sub> model presented at the 2007 SAP (US EPA, 2007). The section summarizes new monitoring data and site information collected since the 2007 SAP and identifies sites that exceed the model effects index LOC (LOC<sub>MEI</sub>) in one or more years using both the CASM<sub>ATZ2</sub>-based and the PATI-based approaches (see Section IV).

### A. Summary of Previous Results

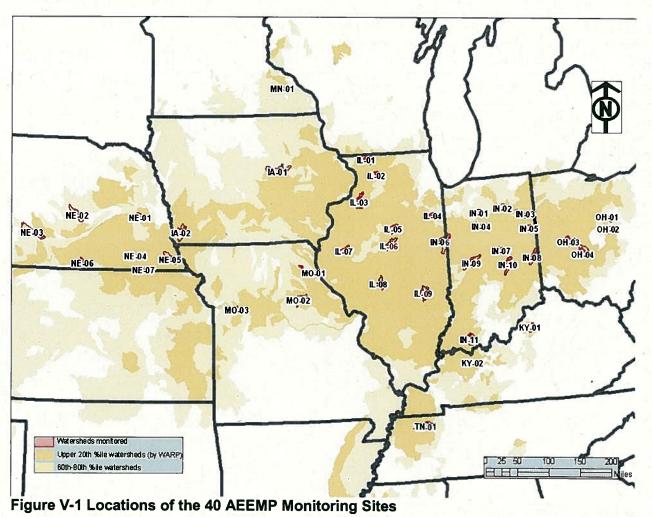
The US EPA's preliminary analysis of the AEEMP monitoring data found that most of the exposures were typified by a high pulse of short duration, a few days or less (USEPA 2007). However, sites that exceeded the LOC for aquatic plant communities had relatively high exposures(though not the highest) of longer duration (i.e. weeks). Two sites (MO-01 and MO-02) exceeded the LOC in multiple years using the CASM<sub>ATZ1</sub>-based approach. In addition, IN-11, with a single high peak (>200  $\mu$ g/L) that quickly returned to baseline concentrations within several days, and three sites in southeastern Nebraska that experienced low flow conditions and missing samples (NE-04, NE-05, and NE-07) exceeded the LOC in one year.

US EPA presented a statistical summary of the watersheds that exceeded the LOC in one or more years, based on the probabilistic nature of the EMAP-based sample design (described in USEPA 2007). The population estimates provided a predictive sense of how many additional locations within the set of vulnerable watersheds might experience similar conditions. Finally, US EPA presented an analysis of the influence of sample frequency on the interpretation of results and proposed an approach for assessing how frequently samples must be collected to be evaluated in the CASM based approach.

The 2007 SAP background document provides a more complete summary of the 2004 to 2007 monitoring data and results (US EPA, 2007).

## **B. Update on Monitoring Data**

In the 2003 design for the AEEMP, 40 monitoring sites were selected from a tier of HUC-10 watersheds identified as vulnerable to atrazine runoff based on the USGS watershed model Watershed Regression on Pesticides, WARP (USEPA, 2007). Figure V-1 shows the locations of the forty sites included in the AEEMP in relation to the extent of those vulnerable watersheds identified by WARP. The dark orange areas represent the upper 20<sup>th</sup> percentile of vulnerable watersheds identified by WARP. The lighter orange areas represent the next most vulnerable tier (60<sup>th</sup> to 80<sup>th</sup> percentile); these watersheds were not included in the site selection but are shown for context. US EPA summarized the monitoring data collected between 2004 and 2006 for the 2007 SAP (USEPA, 2007). Monitoring continued at selected sites and is now available for 2007 and 2008 (see Appendix V-1 for data from 2004 through 2008). In addition, Syngenta added monitoring sites in the vicinity of the Missouri and Nebraska sites of concern to represent watersheds similar to those sites or downstream points at which water exits the larger HUC-10 watersheds. These additional sites provide context to overall exposure and risk conclusions.



The 2003 IRED and addendum specified at least two years of monitoring at the sites, with provisions for additional years for sites that exceeded the LOC or had abnormal rainfall years (US EPA, 2003a, 2003b). While monitoring ended at 29 sites after the 2007 season, the Agency requested that monitoring continue at 11 sites for the following reasons:

- Exceeded the LOC in multiple years: MO-01 and MO-02 using the CASM<sub>ATZ1</sub>-based method (Syngenta also continued monitoring at additional sites MO-04a MO-04b, MO-05 in adjacent sub watersheds)
- Exceeded the LOC in 1 year: IN-11
- Experienced low rainfall during the planting/application period in 1 or more years: IL-03, IL-04, IL-08, IN-06, OH-02
- Missed sampling due to low flow conditions: NE-04, NE-05, and NE-07

#### 1. Sites of Interest

During the 2007 SAP, the US EPA focused on the IN-11, MO-01 and MO-02 sites that exceeded the LOC in one or more years and three "low flow" Nebraska sites (NE-04, NE-05, and NE-07) for which the LOC interpretation was confounded by a large number of missing samples.

Two of the three Missouri sites (MO-01 and MO-02) exceeded the CASM<sub>ATZ1</sub>-LOC<sub>MEI</sub> in three consecutive years of monitoring leading into the 2007 SAP. The chemographs for these sites had broader peak exposures with a longer duration of exposure and lag time between peak and decline to base flow conditions than those of most other AEEMP sites. Syngenta added both downstream integrator sites and sub-watershed sample locations within the larger HUC-10 watersheds for these sites in 2007 and 2008.

The IN-11 site experienced a single peak exposure of 237  $\mu$ g/L during the 2005 sample season. Although the exposure was of short duration (less than 4 days), the chemograph exceeded the CASM<sub>ATZ1</sub>-LOC<sub>MEI</sub>. Subsequent monitoring in 2006 through 2008 yielded lower exposures that were below the LOC. Comparisons of the monitoring results are confounded by lower-than-normal rainfalls and an apparent reduction in corn acreage and atrazine use in the watershed in subsequent years

At the time of the 2007 SAP, the US EPA was still trying to determine whether the large number of missing samples for three southeastern Nebraska sites (NE-04, NE-05, NE-07) were due to an absence of flow (intermittent stream conditions) or to inadequate sampling during low flow conditions (US EPA, 2007). Reported flow rates at these sites (later determined to be estimated flow values) suggested that flow was occurring but at reduced levels. After the 2007 SAP, the US EPA incorporated autosample data, which showed more frequent detections than the grab samples, into the grab sample chemographs. The resulting chemographs exceeded the CASM<sub>ATZ1</sub>-LOC<sub>MEI</sub> in at least one year. Thus, the

Agency asked Syngenta to return to the three southeast NE sites using sampling equipment that would collect water samples during the low flow periods. Similar to the Missouri sites, Syngenta included additional monitoring sites at integrator and additional sub watershed locations.

Chemographs from the additional downstream and integrator sites in Missouri and Nebraska have been evaluated by both the CASM<sub>ATZ2</sub>- and the PATI-based approaches for comparison. Analysis of these additional data provides context to sample results from the 40 AEEMP sites but are not included in the evaluation of the statistical significance of the original probabilistic site sample design.

### 2. Pre- and Post-Sample Period Extrapolation

Because the CASM<sub>ATZ</sub>-based and PATI-based approaches require chemographs with full 365 day profiles, US EPA used a stair-step method to extrapolate concentrations between sampling dates. As described in the December 2007 SAP (USEPA, 2007), measured concentrations are assigned to subsequent non-sampled days until the next sample is collected. To fill in periods before the first sample and after the last sample the Agency carried the concentration detected at the last sample forward through the end of the year and into the next year until the first sample period of that year. When no concentration was available from the previous year, the Agency carried the concentration detected in the first sample back to January 1<sup>st</sup>.

In most cases, the last measured concentration carried forward or backward was low and had no impact on the LOC analysis. However, in a few instances, a relatively high concentration was carried forward or backward. For example, first sample taken at the IN-11 site in 2005 had a detection of 1.93  $\mu$ g/L. The 2007 SAP expressed concern that this represented an unreasonable exposure for the non-sampled period of the chemographs (FIFRA SAP, 2008).

To address this concern, the Agency separated all chemographs into two categories depending on whether the last measured concentration before the pre- or post-sampled period was greater than or less than 0.5  $\mu$ g/L. Although 0.5  $\mu$ g/L was arbitrarily selected, comparison with monitoring data from Heidelberg College suggests it is a reasonable cutoff. Only 20 of 112 chemographs (18%) had concentrations greater than 0.5  $\mu$ g/L at the pre- or post-sampling periods. When the last measured concentration was less than 0.5  $\mu$ g/L, that value was extended through the non-sampled period. Where the last measured concentration was greater than 0.5  $\mu$ g/L, the Agency used 0.29  $\mu$ g/L, which was the 90th percentile value from the distribution of all of the pre- and post-sample exposures that were less than 0.5  $\mu$ g/L. A comparison of these adjusted chemographs with the unadjusted chemographs found slight differences in the risk factors but no differences in risk conclusion (i.e., no change in whether the LOC<sub>MEI</sub> was exceeded). Based on this comparison, the Agency used the adjusted chemographs for all subsequent analyses.

## C. Chemograph Evaluations Based on the CASM and PATI LOC<sub>MEI</sub>S

#### 1. CASMATZ2 LOCMEIS

In the 2007 SAP background document, the US EPA found 2 sites that exceeded the CASM<sub>ATZ1</sub>- LOC<sub>MEI</sub> in multiple years, 1 site that exceeded the LOC<sub>MEI</sub> once, 3 low-flow sites that potentially exceeded the LOC<sub>MEI</sub> once, 2 sites that were within the uncertainty range of the LOC<sub>MEI</sub> , and 32 sites that did not exceed the LOC<sub>MEI</sub> (US EPA, 2007).

The Agency has since analyzed all of the chemographs using the revised CASM<sub>ATZ2</sub> LOC<sub>MEI</sub>. This analysis includes a distributional output that illustrates the impact of the uncertainty (defined in the sensitivity analysis presented in Section IV) on determining which sites have risk factors exceeding the model derived LOC. Table V-1 summarizes the results at the 50<sup>th</sup> and 90<sup>th</sup> percentiles with results exceeding the risk factor of 1.0 highlighted in bold italics.

Table V-1 Summary of AEEMP Risk Factors at the 50th and 90th percentile Using the CASMATZ2- LOCMEI

Site	2004	2005	2006	2007	2008
IA 01	0.25 / 0.851	0.07 / 0.23			Un 15/12-
IA 02	0.34 / 1.00	0.22 / 0.76		1	HE STA
IL 01	0.47 / 1.42	0.04 / 0.13			
IL 02	0.30 / 0.87	0.20 / 0.61	-77 - 4 5 -		
IL 03	9 71 2 1 5 10	0.11 / 0.56	0.06 / 0.25	0.13 / 0.49	
IL 04	1 12 12 13	0.10 / 0.41	0.45 / <b>1.33</b>	0.28 / 1.14	
IL 05	0.30 / 1.52	0.06 / 0.17			
IL 06	0.14 / 0.45	0.02 / 0.08			7
IL 07	0.46 / 2.29	0.10 / 0.29			
IL 08		0.70 / <b>2.02</b>	0.10 / 2.73	0.90 / <b>3.94</b>	
IL 09	0.70 / 1.61	0.35 / 0.72			TE OF THE
IN 01	0.42 / 1.04	0.18 / 0.56			k * 3
IN 02	0.52 / 1.20	0.74 / <b>2.53</b>	Here were		- 7 7 3 4
IN 03	n = 120-1	0.44 / <b>1.01</b>	0.74 / 2.31	15	1 - 1 -
IN 04	0.94 / 7.67	0.43 / <b>1.39</b>	0.52 / <b>1.55</b>		81. 1. 2
IN 05	1.21 / 3.30	0.88 / <b>3.14</b>	1.57 / 5.14		-13
IN 06		0.35 / 0.87	0.53 / <b>1.48</b>	0.24 / 0.60	
IN 07		0.86 / <b>2.10</b>	0.39 / 1.33		.3
IN 08		0.55 / <b>2.19</b>	0.94 / 2.77		
IN 09		0.57 / <b>1.24</b>	0.34 / <b>1.05</b>		
IN 10	• 7=	0.54 / <b>1.31</b>	0.77 / 2.18	÷.	V 50 7 5
IN 11		2.12 / 15.7	0.50 / <b>1.45</b>	0.09 / 0.39	0.43 / <b>1.60</b>
KY 01		0.14 / 0.33	0.53 / <b>2.25</b>		£ 1000
KY 02	-	0.84 / <b>2.35</b>	0.61 / <b>1.71</b>	X - C I	
MN 01		0.41 / <b>1.24</b>	0.03 / 0.10		
MO 01	3.07 / 8.00	5.41 / 21.2	2.72 / 7.55	2.09 / 5.68	1.76 / 7.20

Site	2004	2005	2006	2007	2008
MO 02	2.61 / 7.41	2.00 / 4.43	2.60 / 5.58	0.77 / <b>3.12</b>	1.95 / 6.13
MO 03	1.34 / 5.18	1.04 / 3.31	0.39 / 1.31		
NE 01	0.39 / 2.26	0.77 / <b>2.20</b>		190 10	The su
NE 02		1.46 / 3.22	2.07 / 8.24		
NE 03	0.13 / 0.54	0.28 / <b>1.24</b>			in d
NE 04		2.40 / 5.60	5.02 / 14.2	A P T C PE OF T	3.44 / 12.3
NE 05		2.50 / 5.21	0.53 / <b>2.07</b>	77.	1.19 / 3.75
NE 06	111111111111	1.99 / 5.43	0.02 / 0.08		
NE 07		3.80 / 18.9	0.20 / 0.42		0.97 / <b>5.51</b>
OH 01	0.62 / 2.10	0.19 / 0.53			Land the second
OH 02		0.47 / <b>1.07</b>	0.56 / <b>1.53</b>	0.27 / 1.11	
OH 03	0.70 / 1.97	0.30 / 0.60			
OH 04	L. S. S.	0.52 / <b>1.19</b>	0.20 / 0.62		
TN 01		0.38 / 0.77	0.46 / <b>1.38</b>		

<sup>&</sup>lt;sup>1</sup> The first value is the risk factor at the  $50^{th}$  percentile; the second value is the risk factor at the  $90^{th}$  percentile. Values in bold exceed the LOCMEI (risk factor  $\geq$  1.0).

For the CASM<sub>ATZ2</sub> LOC<sub>MEI</sub>, the risk conclusion depends on the percentile of output selected. The model uncertainty associated with CASM<sub>ATZ2</sub> identified during the sensitivity analysis described in Section IV has a significant impact on the interpretation of each chemograph. Depending on the selected percentile of output, the number of sites with a risk factor greater than 1.0 changes dramatically. At the 50<sup>th</sup> percentile, 10 of the 40 sites had a risk factor greater than 1.0 for any one year, while 36 out of 40 sites had a risk factor greater than 1.0 at the 90<sup>th</sup> percentile (Table V-1).

## 2. PATI LOC<sub>MEI</sub>S

US EPA evaluated the AEEMP data using the PATI LOC<sub>MEI</sub> for all exposure chemographs. Unlike the CASM<sub>ATZ2</sub> LOC<sub>MEI</sub>, the variability in risk factors generated using the PATI LOC<sub>MEI</sub> is limited due to the sensitivity of the model to input values. Regardless of the selected percentile output, the same sites usually exceeded the LOC<sub>MEI</sub>. For example, 8 out of 40 sites exceed the LOC<sub>MEI</sub> in at least one year at the  $50^{th}$  percentile (similar to the median CASM<sub>ATZ2</sub> LOC<sub>MEI</sub> results) while 9 out of 40 sites exceed in at least one year at the  $90^{th}$  percentile (Table V-2). At both percentiles, 3 out of 40 sites exceed the LOC<sub>MEI</sub> in two or more years.

Table V-2 Summary of AEEMP Risk Factors at the 50th and 90th percentile Using the PATI LOC $_{\rm MEI}$ .

Site	2004	2005	2006	2007	2008
IA 01	0.17 / 0.18 <sup>1</sup>	0.06 / 0.06		1 3 12 1	-= -
IA 02	0.19 / 0.20	0.13 / 0.14			11-1:
IL 01	0.35 / 0.37	0.07 / 0.07	2 4		Y = -3,
IL 02	0.21 / 0.22	0.11 / 0.12			
IL 03		0.08 / 0.09	0.05 / 0.06	0.10 / 0.11	

Site	2004	2005	2006	2007	2008
IL 04	e grane in e	0.09 / 0.09	0.29 / 0.30	0.25 / 0.26	E
IL 05	0.26 / 0.30	0.05 / 0.06	.9.6	Tall Unit	
IL 06	0.11 / 0.11	0.04 / 0.04		THE STATE OF	5 FL DE 3
IL 07	0.31 / 0.34	0.0.08 / 0.09		- p	
IL 08	L CHICA L	0.50 / 0.52	0.78 / 0.82	0.79 / 0.81	.V
IL 09	0.63 / 0.66	0.34 / 0.36	13 11	This SETS	W - USCS - T
IN 01	0.33 / 0.34	0.13 / 0.14			A 15 T. o)
IN 02	0.40 / 0.42	0.42 / 0.43	LES SERVICES		7 %
IN 03		0.34 / 0.36	0.55 / 0.56	2 24 - 575.2	
IN 04	0.80 / 0.94	0.20 / 0.21	0.32 / 0.32	714-12 L - 2/	15 15 15 V
IN 05	0.96 / 0.98	0.64 / 0.67	1.04 / 1.07	raft s	1, 1, 1
IN 06	, J L	0.18 / 0.19	0.38 / 0.39	341.4	
IN 07		0.54 / 0.56	0.28 / 0.29	de warr	- 4 4 -
IN 08	. au	0.39 / 0.41	0.61 / 0.63		
IN 09	7 4 12 2	0.42 / 0.44	0.28 / 0.29		
IN 10	A STATE OF THE STA	0.40 / 0.41	0.51 / 0.52		
IN 11	111111111111111111111111111111111111111	1.52 / 1.74	0.50 / 0.51	0.12 / 0.14	0.32 / 0.33
KY 01		0.12 / 0.13	0.24 / 0.28	N ION -	
KY 02	k & Party T	0.65 / 0.68	0.31 / 0.32		
MN 01		0.16 / 0.17	0.03 / 0.03		
MO 01	2.55 / 2.60	3.66 / 3.78	2.29 / 2.32	1.56 / 1.59	0.94 / 1.03
MO 02	2.36 / 2.48	1.62 / 1.74	2.17 / 2.25	0.70 / 0.72	1.06 / 1.10
MO 03	1.13 / 1.18	0.82 / 0.89	0.34 / 0.37	i Troji,	
NE 01	0.59 / 0.60	0.50 / 0.51	dian.	i gran te (2)	7 to 18 to 18
NE 02		0.86 / 0.87	0.96 / <b>1.04</b>		, hi hada kan
NE 03	0.10 / 0.11	0.16 / 0.17			
NE 04		1.90 / 1.92	4.47 / 4.59		3.10 / 3.15
NE 05		2.08 / 2.17	0.33 / 0.35		0.84 / 0.88
NE 06	0.31 / 0.31	0.03 / 0.03	CT of the action	erie i desert	F 11 1
NE 07		3.55 / 3.62	0.26 / 0.28		0.68
OH 01	0.45 / 0.47	0.11 / 0.11		The Rep State	Serie L
OH 02	. Je Carelleane	0.39 / 0.40	0.41 / 0.41	0.19 / 0.19	(Cini Lant
OH 03	0.60 / 0.61	0.19 / 0.20		101	3 V 1 Z
OH 04	FEET-S'	0.37 / 0.39	0.14 / 0.15	11. C et 21.10	+ 4 mal 5
TN 01	AND THE RESERVE	0.41 / 0.44	0.34 / 0.35		1 2 1/2 1/2

<sup>&</sup>lt;sup>1</sup> The first value is the risk factor at the  $50^{th}$  percentile; the second value is the risk factor at the  $90^{th}$  percentile. Values in bold exceed the LOCMEI (risk factor  $\geq 1.0$ ).

# D. Updated Estimates of the Percentage Of Watersheds Exceeding The LOC

The AEEMP monitoring study was designed to estimate the percentage of the vulnerable HUC-10 watersheds in the corn and sorghum growing regions of the United States (represented by the dark orange areas shown in Figure V-1) that are likely to have atrazine concentrations that exceed the LOC in at least one subwatershed. In the 2007 SAP, the Agency estimated that 9 to 11% (ranging from 0

to 24% with a 95% confidence bound) of the vulnerable watersheds would be similar to the 2 MO sites that exceeded the LOC in multiple years. The sites that exceeded the LOC once (IN-11 and the 3 NE low flow sites represented an additional 7 to 9% of the vulnerable watersheds (US EPA, 2007).

In the 2003 monitoring design, Syngenta was unable to find a suitable monitoring site in seven watersheds originally selected for the study and had to move to an alternative site identified for such purposes. Because no inference could be made as to whether these HUC-10 watersheds would have had one or more subwatersheds with LOC exceedances without making additional assumptions, the Agency treated these "excluded" sites as a separate population. Thus, US EPA made two population estimates: one assuming that the watersheds were excluded because of unique characteristics that would have resulted in monitoring chemographs different from the other sites and one assuming that the watersheds were missing at random (USEPA, 2007).

The Agency updated the estimated percentage of watersheds exceeding the LOC with monitoring results through 2008 using the PATI LOC<sub>MEI</sub>.(Table V-3). Assuming that the seven excluded sites represent a separate population of watersheds, 9% of the upper  $20^{th}$  percentile of vulnerable watersheds exceed the atrazine LOC in multiple years (0 to 19% with 95% confidence limits) and 14% exceed the atrazine LOC no more than once in three years (3 to 25%). If the seven excluded sites are missing at random, then 12% of the upper tier of vulnerable watersheds (0 to 25%) exceed the LOC in multiple years and 18% (4 to 31%) exceed the LOC no more than once in three years.

Table V-3 Population Estimates for the Vulnerable Watersheds Based on the AEEMP Monitoring Sites

LOC Category	Number of Sites	Estimated Population %	95% Lower Confidence Bound	95% Upper Confidence Bound
Population Estim	ates Assumii	ng the Excluded S	Sites as a Unique	Subpopulation
Excluded sites	7	22%	10%	33%
Below the LOC	31	55%	45%	66%
Exceeds LOC 1 year	6	14%	3%	25%
Exceeds LOC multiple years	3	9%	0%	19%
Total	47	100%		in a gramma.
Population Esti	mates Assum	ning the Excluded	Sites Are Missin	g At Random
Below the LOC	31	70%	56%	85%
Exceeds LOC 1 year	6	18%	4%	31%
Exceeds LOC multiple years	3	12%	0%	25%
Total	40	100%		

In Section VI, the US EPA provides a spatial context to where these watersheds that have the potential to exceed the LOC in multiple years might occur.

# VI. Identifying Waters That Exceed Effects-Based Atrazine Thresholds Beyond the 40 Sampling Sites

#### A. Preliminary Results and Recommendations from the 2007 SAP

The WARP model used to identify vulnerable watersheds for the AEEMP monitoring site selection estimates percentile concentrations of atrazine based on atrazine use intensity, watershed area, soil erodibility (K) factor, rainfall intensity (R) factor, and Dunne's overland flow (Larson et al, 2004). The 2007 SAP agreed that WARP was a "logical approach" to identifying vulnerable watersheds for monitoring (FIFRA SAP, 2008). While the original design was based on HUC-10 watersheds, both the Agency and the SAP noted that the National Hydrography Dataset (NHDPlus) offers opportunities for refining the vulnerability assessment at a more detailed geographic scale.

The preliminary evaluation of the 2004 to 2006 monitoring data using the CASM<sub>ATZ1</sub>-LOC<sub>MEI</sub> found that two sites in MO (MO-01 and MO-02) exceeded the LOC in multiple years while one site in IN (IN-11) and three sites in NE (NE-04, NE-05, NE-07) exceeded the LOC in one year (US EPA, 2007). US EPA found potential differences in soil and hydrology between the monitoring sites that exceeded the LOC in one or more years and the remaining sites that did not exceed the LOC. In particular, MO-01 and MO-02 occur in a land resource area (Central Claypan Major Land Resource Area, MLRA) characterized by soils with a sharp increase in clay content in the subsurface that results in a dense, slowly permeable subsurface layer that reduces infiltration and drainage (USDA, 1981).

The impact of shallow, drainage-restrictive layers such as a claypan is two-fold:

- A shallow depth to a drainage-restrictive layer reduces the water storage capacity of the soil. During rainfall events, the soil overlying the restrictive layer becomes saturated quickly, increasing the frequency and volume of runoff events in comparison to deeper soils with no restrictive layer in otherwise similar conditions. If the rainfall occurs after atrazine has been applied to the field, the runoff could carry sufficient quantities of atrazine to adjacent streams, resulting in high concentrations.
- Subsurface drainage laterally over the restrictive layer would result in a delayed baseflow, contributing additional loadings of atrazine over time, prolonging the exposure period in the receiving water bodies.

The US EPA proposed to identify the watershed attributes (atrazine use, soils, hydrology, weather) that distinguish monitoring sites that exceeded the LOC from those that do not (USEPA, 2007). These characteristics would then be used to identify other watersheds outside of the original monitoring sites with similar attributes. Further, because some of the soil/hydrologic parameters the Agency planned to evaluate were not explicitly part of the WARP parameters, the evaluation

would extend beyond the original high-vulnerability tier of watersheds defined by WARP to include the broader atrazine use area.

The SAP noted that "since vulnerability is a combination of the physical setting and the land use, the best approach would be to build on the idea that vulnerable watersheds have specific soil characteristics in combination with some minimum atrazine use criteria (or minimum corn and sorghum acreage)" (FIFRA SAP, 2008; p. 35). The SAP made the following recommendations regarding the US EPA's proposed watershed evaluation and extrapolation approach:

- Update the hydrologic framework to NHDPlus to address some of the limitations of interpreting monitoring results from sites located within HUC-10 watersheds.
- Use the Soil Survey Geographic (SSURGO) and NHDPlus databases to incorporate more soil- and hydrology-related parameters to more fully capture the potential causal factors driving atrazine exposure.
- Use the most up-to-date atrazine use data possible, both spatially and temporally.
- Add other existing monitoring sites to the database, if possible, to include a representative range of scales for streams.
- Update WARP using the additional soil and hydrologic factors and expand the scale of analysis to the entire Corn Belt.

Based on this feedback from the 2007 SAP, the Agency incorporated additional soil and hydrologic factors with updated atrazine use information to identify watershed characteristics that might distinguish the monitoring sites that exceed the atrazine LOC from those that do not exceed the LOC. US EPA used the results of this analysis to identify other watersheds within the atrazine use area that had similar characteristics. The analysis used the NHDPlus catchments as the framework for identifying watershed characteristics upstream of the monitoring sites.

# B. Watershed Factors Driving Atrazine Exposures in the AEEMP Study

Using the PATI LOC<sub>MEI</sub> described in Section IV of this document, US EPA grouped the monitoring sites into three LOC categories based on the results of the monitoring study (Section V):

- 3 sites that exceeded the LOC in multiple years: MO-01, MO-02, NE-04
- 6 sites that exceeded the LOC in one year only: IN-05, IN-11, MO-03, NE-02, NE-05, NE-07
- 31 sites that never exceeded the LOC during the sampling period

US EPA used the upstream drainage area tool to aggregate the individual NHDPlus watersheds (HSC, 2006) into the upstream catchment area for each of the 40 AEEMP monitoring stations. These upstream catchments ranged from 20 to 167 km² in size, compared to the 32 to 863 km² range for the corresponding HUC-10

watersheds. While the original HUC-10 datasets included information on drainage areas downstream from the actual monitoring sites, the aggregated NHDPlus catchment areas reflect only the characteristics of the upstream areas that would impact the monitoring site.

EPA looked for watershed characteristics, singly or in combination, that characterized the sites in the three LOC categories, with particular emphasis on differences between the 3 sites that exceeded the LOC in multiple years and the 31 sites that did not exceed the LOC during the sampling period. This section highlights the pesticide use, soil, hydrologic, weather, and watershed parameters that contributed to explaining the differences among the LOC categories. Appendices VI-1 (atrazine use data) and VI-2 (soil, hydrology, and weather data) describe how the data were derived and provide more detailed watershed characteristics.

#### 1. Pesticide and use parameters

In developing the WARP model, Larson et al. (2004) found that atrazine use intensity (mass of pesticide used per watershed area) explained 62 to 77% of the variability in atrazine concentrations in streams. The 2007 SAP, noting the importance of accurately characterizing use on both a spatial and temporal scale, recommended that the US EPA obtain updated atrazine use data at the most detailed level possible (FIFRA SAP, 2008).

Syngenta provided the US EPA with updated atrazine use data for the entire corn- and sorghum-growing region covering 2004 through 2007 (Appendix VI-1). Syngenta used Doanes survey data to estimate atrazine application rates reported by farmers across the country. Although the Doanes pesticide use data are reported for multi-county crop-reporting districts that are much larger in scale than the monitoring site catchments, they represent one of the few sources of pesticide usage data collected yearly on a national scale. While the 2007 SAP suggested acquiring herbicide sales data similar to a program used by the State of Iowa (FIFRA SAP, 2008), such programs are not yet widely available or consistent across the atrazine use area.

Syngenta estimated atrazine usage at an NHDPlus-catchment scale by:

- (1) Calculating an atrazine application rate in pounds of active ingredient per base acre of corn and sorghum treated (lb ai/A) for each crop reporting district using Doanes 2004-2007 usage data.
- (2) Estimating the percent of the catchment in corn and sorghum using the best available crop data. For the majority of the Midwest, lower Mississippi Valley, and Pacific Northwest, the USDA NASS cropland data layer (USDA NASS, 2007) provided crop-specific data at 56-m resolution. Corn and sorghum are identified separately. In other parts of the country, Syngenta used a combination of the 2007 USDA NASS crop survey, 2002 Agricultural Census,

- and 2001 National Land Cover Dataset (NLCD) to estimate corn and sorghum acres in the watershed.
- (3) Joining the atrazine use rate from Doane's with the percent corn/sorghum acres in the catchment to calculate an average atrazine use intensity over the 2004-2007 period for the catchment in pounds of active ingredient per catchment acres.

Syngenta also provided year-to-year estimates of atrazine use for the catchments associated with the 40 monitoring sites (Appendix VI-1). This information was useful in analyzing the year-to-year variability in monitoring results but was not used in the overall watershed analysis because the year-to-year variability in use intensity was based on estimates of the percent corn and sorghum in the watershed using land cover estimates that were not consistent across the monitoring sites or years (Appendix VI-1). For instance, while the estimated use intensity for IN-11 in 2006 and 2007 was 50 to 60 percent of the intensity in 2005 when it exceeded the LOC, the estimates are derived from different cropland data sources, which introduce additional uncertainty to the estimates.

The monitoring sites that exceeded the LOC in one or more years did not necessarily have the highest atrazine use intensities (Figure VI-1) or the highest percentages of corn and sorghum in the upstream catchments (Figure VI-2).

Because the site selection process used WARP to identify an upper tier of vulnerable watersheds, the variability in atrazine use intensity may be narrower than in watersheds selected entirely at random across the entire corn belt, including low- or no-use areas. Nevertheless, these monitoring sites reflect a range of use intensities from as low as 0.05 lb ai/A (KY-01) to as high as 0.72 lb ai/A (IL-08). Use intensities ranged from 0.32 to 0.45 lb ai/A for the three sites that exceeded the LOC in multiple years to as low as 0.10 lb ai/A for the sites that exceeded the LOC in one year. In the original watershed monitoring design, the initial pool of watersheds in the WARP vulnerability assessment included all areas that intersected counties with a minimum atrazine use intensity of 0.25 lb ai/A. The atrazine use intensities in Figure VI-1 reflect more recent atrazine use in the watersheds during the monitoring study.

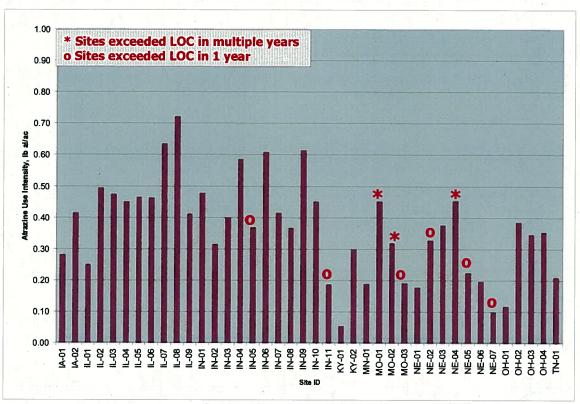


Figure VI-1 Atrazine use intensity, Ib ai/ catchment acre, for the 40 AEEMP monitoring sites

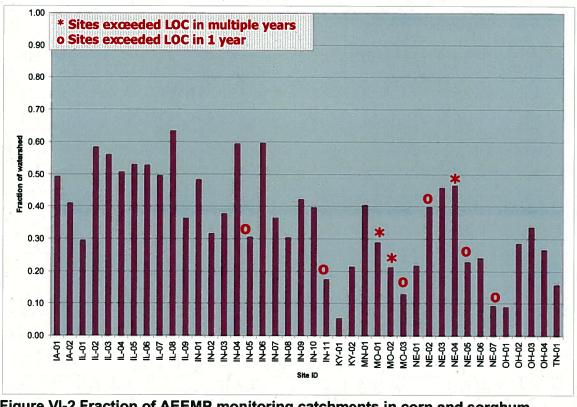


Figure VI-2 Fraction of AEEMP monitoring catchments in corn and sorghum

The percentage of the upstream catchment area in corn and/or sorghum ranged from 5% for KY-01 to 63% for IL-08 (Figure VI-2). Of the sites that exceeded the LOC in multiple years, the two MO sites had 21-29% corn and sorghum in the upstream catchment while NE-04 had 46%.

While atrazine use and/or corn/sorghum intensity in the watershed are important factors contributing to the atrazine concentrations seen in streams, these factors alone do not sufficiently account for the differences in exposures seen among the monitoring sites in the AEEMP study.

#### 2. Evaluation of Soil-Related Parameters

The chemographs that triggered the LOC in the monitoring study had relatively high atrazine concentrations with prolonged periods of elevated exposures. Syngenta attributed the prolonged periods of elevated exposure in MO-01 and MO-02 to the presence of 'claypan' soils in the region (Hampton et al, 2007a, b). Additional research conducted by the USDA in the Central Claypan MLRA, where the watersheds are located, came to similar conclusions (Blanchard and Lerch, 2000; Lerch and Blanchard, 2003). The US EPA noted that prolonged exposures may result from a range of soil restrictive layers (USEPA, 2007).

"Claypan" is a generic term for a subsurface soil layer that has a sharp increase in clay content compared to overlying layers. This results in a dense, slowly permeable subsurface that reduces infiltration and drainage (USDA, 1981). USDA NRCS defines a restrictive layer as a "nearly continuous layer that has one or more physical, chemical, or thermal properties that significantly reduce the movement of water and air through the soil or that otherwise provide an unfavorable root environment" (USDA NRCS, 2007).

Soil restrictive layers defined by USDA have not been included in all of the SSURGO survey areas available through the USDA Soil Data Mart (USDA NRCS, 2008) at the time of this analysis. Therefore, US EPA considered a variety of soil and hydrologic factors that could be used to identify both drainage-restrictive layers and other factors that might contribute to the vulnerability of watersheds to atrazine runoff into streams (Table VI-1).

Table VI-1 Soil properties derived from SSURGO used in the analysis of catchments upstream of the AEEMP monitoring sites.

Soil Property	Parameter		
Saturated Hydraulic Conductivity (Ksat), Surface	% watershed area with surface Ksat values <1 um/s		
Surface Organic Matter (OM) Content	% watershed area with surface OM matter content <1% watershed area with surface OM content<2% watershed area with surface OM content<3%		
Clay Content, Depth to Clayey Subsurface Layer	% watershed area with > 40% clay within 25, 50, or 100 cm of the surface		

Soil Property	Parameter
Saturated Hydraulic Conductivity, Depth to Restrictive Ksat	% watershed area with Ksat <1 um/s within 25, 50, or 100 cm of the surface % watershed area with Ksat <0.5 um/s within 25, 50, or 100 cm of the surface % watershed area with Ksat <0.25 um/s within 25, 50, or 100 cm of the surface % watershed area with Ksat <0.1 um/s within 25, 50, or
Soil Runoff Class	100 cm of the surface % watershed area in Very High and High runoff classes
Hydrologic Soil Groups	% watershed area in hydrologic group D soils % watershed area in hydrologic group C+D soils % watershed area in hydrologic group D + (A/D, B/D, C/D) soils
Slope Gradient	Watershed area weighted average slope gradient, % watershed area in 2-8% and 8-15% slopes
Natural Soil Drainage Class	% watershed area in well (W) drained, moderately-well (MW), and somewhat-poorly (SWP) drained soils
Available Water Storage (AWA) Capacity	Watershed area-weighted average AWS, upper 25 cm Watershed area-weighted average AWS, upper 50 cm Watershed area-weighted average AWS, upper 100 cm Watershed area-weighted average AWS, upper 150 cm
Soil Erodibility (K) Factor	Watershed area-weighted average K factor

While the soil properties listed in Table VI-1 are not independent of each other, each reflects aspects not fully captured by the others. A soil layer high in clay may suggest a drainage restriction, but factors such as mineralogy, soil structure. and organic matter content also impact drainage. Saturated hydraulic conductivity (Ksat), a measure of how quickly water moves through soil, is a function of the arrangement and size distribution of pores in the soil, which is influenced by soil texture, organic matter content, soil structure, and bulk density. Soil runoff class is a function of slope gradient and Ksat of the surface and nearsurface layers. Hydrologic soil group classification is a function of Ksat and the depth to free water occurrence (water table). Soil drainage class reflects the frequency and duration of wet conditions and is affected by Ksat, soil texture (%sand, silt, clay), and depth to water table. Available water storage (AWS) is a function of soil porosity, soil texture, and organic matter content, (USDA SSDS. 1993) In evaluating these soil properties, the Agency considered not only the additional information provided by each parameter, but the interdependencies among the properties.

Greater than 70 percent of the catchment areas upstream of the three monitoring sites that exceeded the LOC in multiple years had soils with a high-clay subsurface (defined as having greater than 40% clay) within 50 cm of the surface (Figure VI-3). Three of the six sites that exceeded the LOC in one year had soils with a shallow high-clay subsurface covering greater than 60% of the watershed, while the other three had relatively little high clay soils in the watershed.

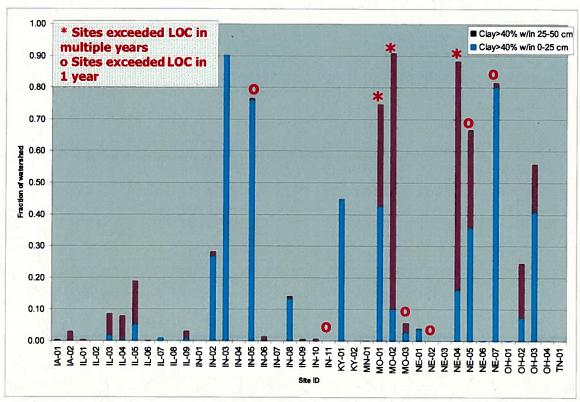


Figure VI-3 Fraction of AEEMP watersheds with a high clay layer within 50 cm of the surface

All but three of the sites that did not exceed the LOC had high-clay soils covering less than 30% of the watersheds. While the IN-03 site had soils with a high clay subsurface covering 90% of the catchment area, these soils did not have low saturated hydraulic conductivities (Figure IV-4). Similarly, the high-clay soils found in IN-02, KY-01, OH-02 and OH-03 did not have correspondingly low Ksat values.

Greater than 67% of the catchments for the three sites that exceeded the LOC in multiple years contained soils that had a Ksat value of less than 1  $\mu$ m/s within 50 cm of the surface (Figure VI-4). Two additional NE sites that exceeded the LOC once (NE-05 and NE-07) also had a high proportion of soils with a low subsurface Ksat layer. A comparison of Figure VI-3 and Figure VI-4 indicates that the presence of a high-clay subsurface is not a sufficient indicator of a drainage restriction. Ksat values are needed to identify soils with shallow drainage-restrictive layers that may contribute to atrazine runoff in streams. The majority of the shallow restrictive layers in NE-04, NE-05, and NE-07 had Ksat values of less than 0.25  $\mu$ m/s, while the majority of soils in MO-01 and MO-02 had Ksat values of less than 1  $\mu$ m/s but greater than 0.25  $\mu$ m/s within 50 cm of the surface (see Appendix VI-2),

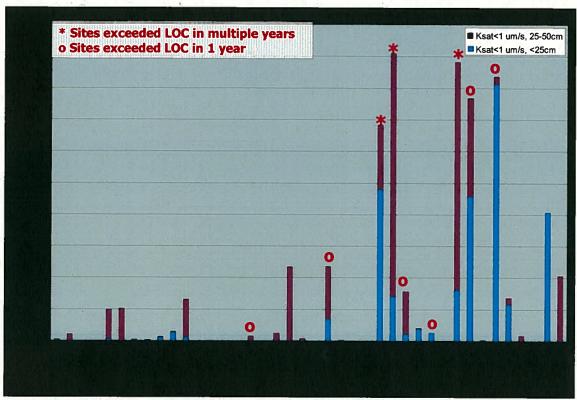


Figure VI-4 Fraction of AEEMP watersheds with Ksat <1 μm/s within 50 cm of the surface

US EPA found no evident trends in slope gradient between the catchments that exceeded the LOC and those that did not based on an analysis of the SSURGO mapping units (see Appendix V-2). Although other sources, such as the digital elevation model (DEM), may provide more detailed slope and elevation data, the impacts of slope gradient on atrazine runoff to streams may be linked with other properties or may reflect a threshold value (i.e., a minimum average slope gradient or minimum percentage of watershed above a certain slope gradient). Additional geomorphic features that might amplify the contribution of slope on runoff, such as surface contour and landform, were not included in this analysis.

Lerch and Blanchard (2003) observed that herbicide loss rates tended to increase with increasing runoff potential of soils. Areas with greater than 70% hydrologic group C and D soils had a high pesticide runoff propensity, while areas with less than 30% hydrologic group C and D soils had a low runoff propensity (Blanchard and Lerch, 2000).

All three sites that exceeded the LOC in multiple years had greater than 85% hydrologic group C and D soils in the upstream catchments; five of the six sites that exceeded the LOC in one year had greater than 60% C and D soils (Figure VI-5). Hydrologic group D soils comprised greater than 60 percent of the catchments for the MO-01, MO-02, NE-05, and NE-07 and 20 percent of the catchment for NE-04. Seven sites that did not exceed the LOC also had

hydrologic group C and D soils covering greater than 70 percent of the catchment, but only TN-01 had more than 20 percent hydrologic group D soils.

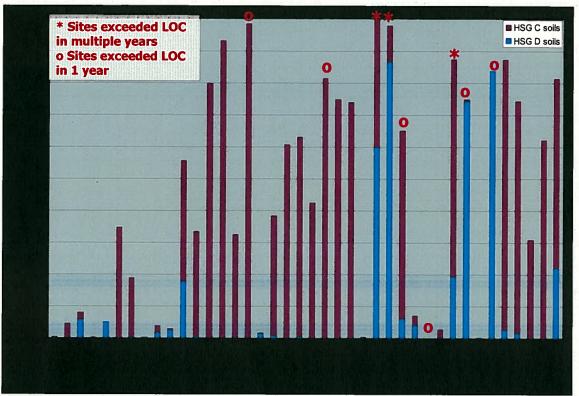


Figure VI-5 Fraction of AEEMP watersheds containing hydrologic group C and D soils

The USDA NRCS index surface runoff class integrates saturated hydraulic conductivity and slope to rate soils according to their potential for surface runoff (USDA SSDS, 1993). At least 50 percent of the catchment area for sites that exceeded the LOC in multiple years and 40 percent of the catchment area for sites that exceeded the LOC in one year consisted of soils with a high or very high runoff potential (Figure VI-6). Only one site that did not exceed the LOC had high runoff potential soils covering greater than 50 percent of the watershed (NE-01). While soils with very high runoff potential occupied greater than 60 percent of the MO-01 and MO-02 catchments, similar conditions only occurred in 5 percent of the NE-04 catchment.

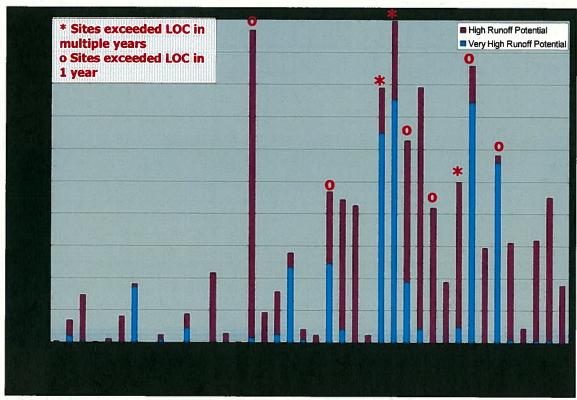


Figure VI-6 Fraction of AEEMP watersheds containing soils with high or very high runoff potential

## 3. Evaluation of Weather and Hydrology Parameters

In addition to the soil factors mentioned in Table VI-1, US EPA considered weather and hydrology factors that might impact atrazine exposure in streams. The three sites that exceeded the LOC in multiple years and four of the six sites that exceeded the LOC in a single year are located in northeastern MO and southeastern NE, at the lower end of the average annual and monthly precipitation (Figure VI-7) and rainfall intensity (R factor) within the study area (Figure VI-8). The Agency's previous analysis of on-site rainfall distributions during the monitoring study indicates that the relationship between atrazine concentrations in streams and precipitation is a function of the distribution and timing of the rainfall in relation to application rather than to the amount of rainfall in a given month or season. The US EPA's analysis of rainfall and atrazine concentrations for the 2004-06 monitoring years found that the amount of rainfall during the application months did not correspond to atrazine concentrations in the stream. Some of the higher measured atrazine concentrations occurred at sites during periods with lower monthly rainfalls. The timing of rainfall events and stream flow at the time of the runoff event were more critical factors explaining the atrazine concentrations in the streams (US EPA, 2007). The overall trend indicates that, like atrazine use, a minimum threshold on rainfall amount exists. Above that threshold, soil factors drive the vulnerability.

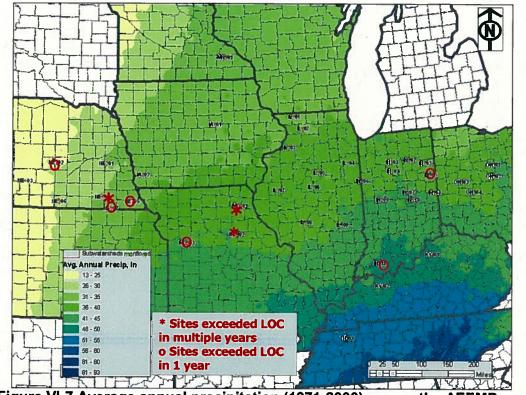


Figure VI-7 Average annual precipitation (1971-2000) across the AEEMP area

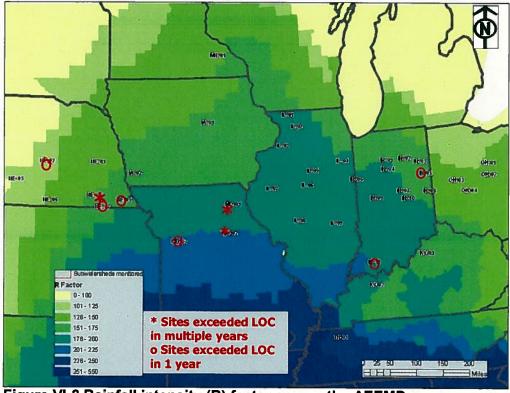


Figure VI-8 Rainfall intensity (R) factor across the AEEMP area

US EPA also looked at two hydrologic factors that were included in USGS's development of the WARP model (Larson et al, 2004):

- The percentage of total streamflow in the watershed that is due to overland flow from saturated soils (also known as Dunne's overland flow)
- The percentage of total streamflow in the watershed that is due to overland flow that occurs when rainfall exceeds infiltration (also known as Horton's overland flow)

These parameters were calculated using TOPMODEL (Wolock, 2003a, 2003b) and were included in the development of the WARP model (Larson et al, 2004). Appendix VI-2 summarizes those hydrologic factors by monitoring site.

The Agency compared the average stream flow reported for each site and year by Syngenta but found no discernable flow trend between sites that exceeded the LOC and those that did not (Appendix VI-2).

### 4. Characteristics of Sites That Exceed the Atrazine LOC

US EPA analyzed various upstream catchment characteristics described in the previous sections to identify watershed characteristics that best distinguished between sites that exceed the atrazine LOC and those that do not. The presence of high or very high runoff potential soils or of hydrologic group C and D soils can be used to identify areas which are vulnerable to atrazine runoff into streams. Within those runoff-vulnerable watersheds, the presence of soils with a shallow depth to a drainage restrictive layer, indicated by a low Ksat value, can be used to identify those areas where subsurface flow laterally over the restrictive layer would contribute additional loadings of atrazine over time, prolonging the exposure period in the receiving water bodies.

Hydrologic group C and D soils comprised greater than 60 percent of the catchments upstream of all three sites that exceeded the LOC in multiple years (MO-01, MO-02, NE-04) and five of the six sites that exceeded the LOC in a single year (IN-05, IN-11, MO-03, NE-05, NE-07) (Figure VI-5). The catchment area for the sixth site, NE-02, was comprised almost entirely of hydrologic group B soils. Eleven sites that did not exceed the LOC during the study period also had greater than 60 percent hydrologic group C and D soils in the upstream catchment area.

Soils with high to very high runoff potential comprised greater than 40 percent of upstream catchments for all three sites that exceeded the LOC in multiple years and all six sites that exceeded the LOC in a single year (Figure VI-6). The 40 percent cutoff for high runoff potential soils also included four sites that did not exceed the LOC during the study period.

The Agency used Ksat of less than 1 µm/s within 50 cm of the surface to identify shallow, drainage-restrictive layers in the soil. Soils with a shallow depth to a

drainage restrictive layer comprised 67 to greater than 90 percent of the area upstream of the three sites that exceeded the LOC in multiple years. None of the sites that did not exceed the LOC had shallow restrictive layers occupying greater than 41 percent of the upstream catchment.

The presence of runoff prone soils, as indicated by the USDA runoff class or hydrologic soil group, characterizes sites that have the potential to exceed the atrazine LOC on occasion (symbolized by those sites that exceeded the LOC once in three years of sampling). The presence of soils with a shallow restrictive layer characterizes those sites that exceed the LOC in multiple years.

Figure VI-9 illustrates the application of the criteria for hydrologic soil groups (≥60 percent C or D soils), runoff (≥40 percent high or very high), and depth to Ksat of less than 1 μm/s within 50 cm of the surface (≥45 percent) to the forty AEEMP monitoring sites. The three sites that exceeded the LOC in multiple years and two additional sites in southeastern NE (NE-05 and NE-07) met the combined high runoff / shallow restrictive layer criteria.

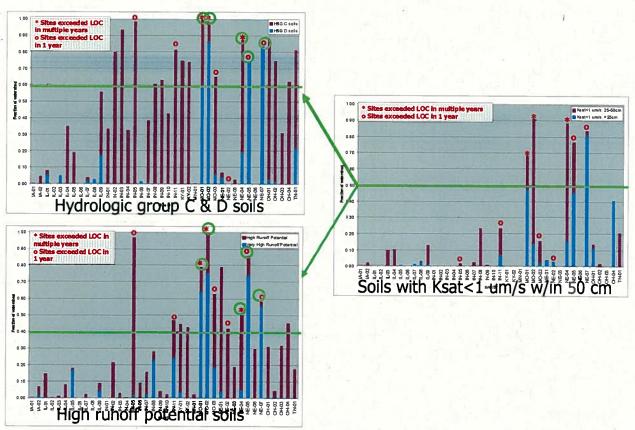


Figure VI-9 Application of criteria for identifying sites that exceed the atrazine LOC based on the presence of high runoff soils and shallow restrictive layers in the watershed

Neither atrazine use intensity nor the percent of the watershed in corn or sorghum show obvious patterns between sites that exceeded the LOC in one or more years and those that did not exceed during the study period. The

relationship between rainfall amount, timing, and intensity and atrazine concentrations in streams is more complex than can be easily captured in seasonal or monthly average precipitation totals (US EPA, 2007). The amount and timing of individual rainfall events relative to the timing of atrazine use in the watershed, rather than annual or monthly rainfall averages, is a better indicator of atrazine concentrations in streams (US EPA, 2007).

The results suggest that a minimum threshold exists for atrazine use intensity and rainfall amount/intensity; above that threshold, soil factors drive the vulnerability to atrazine exposure in streams. In the AEEMP study, sites that exceeded the LOC in at least one year had a use intensity as low as 0.10 lb ai/A or at least 10 percent corn/sorghum in the upstream area. Among the sites that exceeded the LOC in one or more years, the minimum annual agerage rainfall is 23 inches and the minimum combined average April-May rainfall is 6.3 inches.

# C. Identifying Watersheds with Characteristics Similar to Those That Exceed the Atrazine LOC

The US EPA used the results of the watershed analysis in Section VI.B to identify other watersheds within the atrazine use area that are similar to the sites that exceeded the atrazine LOC in multiple years. Watersheds that may exceed the atrazine LOC for ecological effects were identified based on the following soil parameters, compiled for NHDPlus catchments:

- 1) Define the extent of potential vulnerable watersheds based on atrazine use intensity and rainfall:
  - Atrazine use intensity within the catchment is at least 0.1 lb ai/A or corn or sorghum use occupies at least 10 percent of the catchment, and
  - Average annual rainfall is at least 23 inches or average April-May precipitation is at least 6 inches; this excluded areas in western KS and NE northward to northwestern MN (Figure VI-7)
- 2) Within this area, identify watersheds that are vulnerable to runoff based on one of the following criteria:
  - Soils with a very high or high runoff potential comprise at least 40 percent of the catchment area, or
  - Hydrologic group C or D soils comprise at least 60 percent of the catchment area,
- 3) Among the runoff-vulnerable watersheds, identify areas that have soils with a shallow restrictive layer based on the following criteria:
  - Soils containing a subsurface layer with a Ksat value of ≤1 µm/s within 50 cm of the surface comprise at least 45 percent of the catchment area

While the presence of soils with a high or very high runoff potential may be a better identifier of watershed vulnerability to runoff, the runoff parameter was not included

for every map unit in each of the SSURGO survey areas at the time of this assessment. Therefore the hydrologic soil group criterion serves as an alternate indicator where the runoff parameter has not been provided.

Figure VI-10 shows the extent of watersheds in a 10-state region (OH, KY, TN, IN, IL, MN, IA, MO, NE, KS) with characteristics similar to those that exceeded the atrazine LOC in multiple years in the AEEMP study. The green to gray shades on the map depict areas that meet the high runoff and shallow restrictive layer criteria where annual precipitation is greater than 23 inches. Within these vulnerable soil areas, the dark green areas have an estimated atrazine use intensity greater than or equal to 0.1 lb ai/A. The light green areas have an atrazine use intensity of greater than 0 but less than 0.1 lb ai/A. Gray areas meet the soil criteria but had no corn or sorghum grown in the watershed. The dark orange background shows the extent of vulnerable watersheds identified by WARP that were represented by the 40 AEEMP monitoring sites. The light orange shows the extent of the next lower tier of vulnerable watersheds.

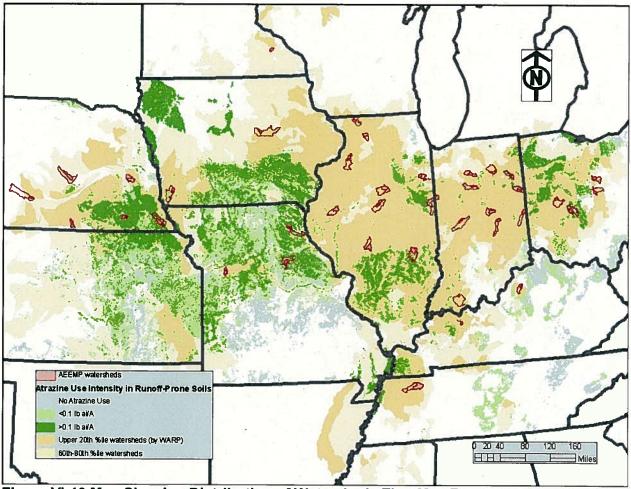


Figure VI-10 Map Showing Distribution of Watersheds That May Exceed the Atrazine LOC Based on Atrazine Use, Precipitation, and Soil Criteria.

As expected from the AEEMP study, a large portion of the Central Claypan MLRA in northeastern MO (where MO-01 and MO-02 are located) and in southern IL meet the soil and use criteria (Figure VI-10). The dark green areas in southern IA are part of the lowa and Missouri Heavy Till Plain MLRA. The soils in this MLRA formed in a layer of silty loess that covers high-clay glacial till that can serve as a restrictive drainage layer when close to the surface (USDA, 1981).

Another area with a relatively high proportion of high runoff, drainage restrictive soils occurs in southeastern Nebraska, extending southward into east central Kansas (Figures VI-10 and VI-11). Three AEMP sites that exceeded the LOC in one or more years occur in the dark green (high atrazine use) areas of southeastern NE (NE-04, NE-05, and NE-07). While eastern Kansas has a high proportion of vulnerable soils, the atrazine use intensity is generally low in most of these areas. The dark green areas that correspond to high atazine use in vulnerable soil conditions are associated with upper tier of vulnerable watersheds identified by WARP, while the light green (low use) and gray (no use) areas are associated with less vulnerable watersheds (Figure VI-11).

Smaller areas where high runoff, drainage restrictive soils coincide with high atrazine use occur in northeastern Illinois, western Kentucky, and western Ohio (Figure VI-10). These areas are largely associated with the upper tier of vulnerable watersheds represented by the AEEMP monitoring sites. Thus, while the soil criteria associated with the sites that exceeded the LOC were not explicitly accounted for by the original WARP model, the vulnerable watersheds identified by those soil characteristics are predominantly associated with that most vulnerable tier of watersheds.

# D. Evaluating Vulnerable Watershed Criteria with Monitoring Data Not in the AEEMP

The US EPA plans to use additional atrazine monitoring data beyond the AEEMP study to evaluate the results of the watershed analysis in Sections VI.B and VI.C in identifying areas similar to the AEEMP sites that exceed the atrazine LOC. Monitoring data sets to be used by US EPA include recent data provided by state water and/or pesticide agencies in Nebraska, Kansas, Iowa, Minnesota, California, Montana, and Florida; USDA ARS monitoring in Missouri; Heidelberg College monitoring in OH; USGS NAWQA monitoring covering 2004-07; and data collected by Syngenta at Community Water Systems (CWS) as a part of a separate drinking water monitoring program required by the 2003 IRED. Where the sampling frequency is sufficient frequency (at least bi-weekly, often more frequently during the growing season), USEPA will evaluate the chemographs using the PATI LOC<sub>MEI</sub>. For data that were sampled less frequently, US EPA will look at the magnitude of atrazine concentrations detected in the samples.

This section provides a brief description of the monitoring data sets and a preliminary evaluation of the watershed criteria using these data. At the time of publication of this paper, US EPA has not yet analyzed surface water monitoring

data from the lowa Department of Agriculture or from NAWQA. The Agency plans to incorporate these data sets into the analysis and will update the SAP during the May 2009 meeting. The monitoring data can be found in Appendix VI-3.

### 1. Description of Monitoring Data Sets

**Nebraska:** The Nebraska Department of Environmental Quality (NDEQ) provided surface water monitoring data collected as part of both its ambient stream monitoring program and the Blue River Basin Water Quality Source Assessment (NDEQ, 2008). The monitoring data, collected between 2004 and 2006, represent one of the most robust atrazine data sets in terms of sample locations (targeted to atrazine use) and frequency (samples collected typically every two weeks during the growing season and occasionally more frequently). US EPA evaluated the chemographs for a subset of sites that had detections greater than 20 μg/L and at least biweekly sample frequencies using the PATI LOC<sub>MEI</sub> (Table VI-2). The 26 sites that exceeded the LOC in one or more years are located in the southeastern portion of Nebraska (Figure VI-11**Error! Reference source not found.**).

Kansas: The Kansas Department of Health and Environment (KDHE) provided US EPA with monitoring data across the state covering many years (KDHE, 2008). While the sample frequency is limited with no more than 4 to 6 samples collected in a given year, the data provide context based on locations of with atrazine detections greater than 20  $\mu$ g/L. The maximum detection in the study was 63  $\mu$ g/L in 1997; the maximum detection since 2004 (when the AEEMP was initiated) was 49  $\mu$ g/L. Of the 361 stations with geographic locations, 25 stations had detections greater than 20  $\mu$ g/L, mostly located in eastern KS (Figure VI-11).

**Minnesota:** The Minnesota Department of Agriculture (MnDA) provided results of recent monitoring data for nine sites in southern Minnesota representing a high atrazine use area for the state (MnDA, 2008). Samples were collected frequently during the peak use season, approaching daily intervals during peak periods between May and July. The US EPA analyzed the chemograph with the highest atrazine concentrations (Middle Branch of the Whitewater River) using the PATI LOC<sub>MEI</sub> (Table VI-2). This site did not exceed the LOC; it is therefore expected that the other sites would not exceed either.

California: The California Department of Pesticide Regulations (CDPR) measured atrazine detections in 550 samples out of nearly 5,000 monitoring samples taken between 1991 to 2008 (CDPR, 2008). None of the sites were sampled frequently enough to evaluate using the PATI LOC<sub>MEI</sub>. However, only 5 had detections greater than 1  $\mu$ g/L, with a maximum detection of 5.3  $\mu$ g/L. None of these exposures are expected to exceed the LOC.

**Montana:** The Montana Department of Agriculture (MtDA) found no atrazine concentrations above the limit of quantitation in 220 samples collected between 2006 and 2008 (MtDA, 2008).

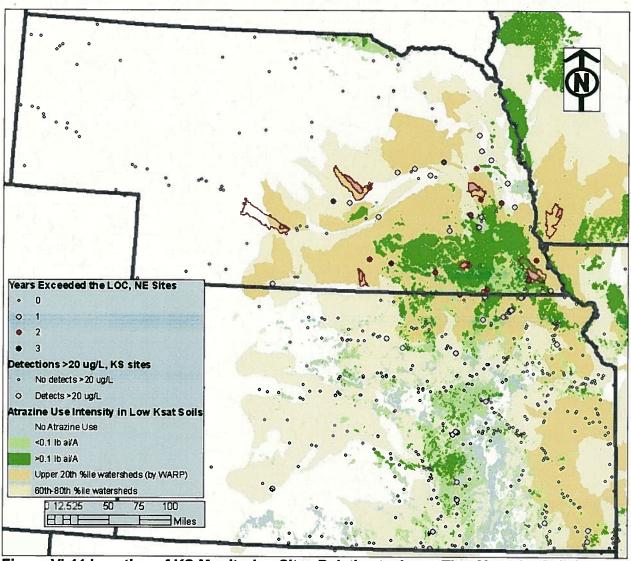


Figure VI-11 Location of KS Monitoring Sites Relative to Areas That Meet the Soil Criteria

**Florida:** The Florida Department of Agriculture and Consumer Services (FDACS) found atrazine detections in two-thirds of over 3,800 samples extracted from STORET, spanning the mid 1980s to 2006. Only 350 samples were greater than 1  $\mu$ g/L; only 7 were greater than 10  $\mu$ g/L (all before 2001), with a maximum detection of 18  $\mu$ g/L in 1993. While a limited sample frequency precluded using the PATI LOC<sub>MEI</sub>, the low frequency of detections and low concentrations suggest that these sites are not likely to exceed the LOC<sub>MEI</sub>.

**USDA-ARS (Columbia, MO):** The USDA ARS field office in Columbia, MO, provided the US EPA with data collected within the Goodwater Creek watershed between 2003 and 2006. The site, referenced in the FIFRA SAP (2008) report, is

located near MO-02, although not specifically within the same subwatershed. Analysis of the chemographs with the PATI LOC<sub>MEI</sub> yielded Risk Factors consistent with those from the AEEMP data set (Table VI-2).

**Heidelberg College (OH):** The Agency analyzed the Heidelberg College surface water data used in the original development of the CASM<sub>ATZ</sub> model (REF). The dataset includes 48 chemographs sampled between 1987 and 2002 from 9 sites in Ohio. Because these chemographs are from an earlier timeframe than the AEEMP, they likely do not represent current use patterns and application rates for atrazine, However, they can be used to evaluate intrinsic soil/site parameters contributing to the vulnerability of streams to atrazine levels that exceed the LOC. Honey Creek and Sandusky River exceeded the PATI LOC<sub>MEI</sub> in multiple years, while Lost Creek, Maumee, Miami, Raisin, Rock, and Scioto rivers exceeded the LOC in one year (Table VI-2).

Atrazine Monitoriong Program (AMP) Community Water Systems (CWS): As part of the IRED memorandum of agreement (US EPA, 2003b), the US EPA required Syngenta to monitor CWS in the principal triazine use area of the US midwest. The AMP samples roughly 120 to 140 CWS each year with intensive sampling during the principal use season. The US EPA selected a subset of CWS that had detections greater than 20  $\mu$ g/L for analysis using the PATI LOC<sub>MEI</sub> (Table VI-2).

Table VI-2 Summary of Risk Factors based on the PATI LOC $_{\rm MEI}$  for Monitoring Sites Not in the AEEMP

Site	2003	2004	2005	2006	2007
BUNGAL COLOR BUNGAL PROPERTY	State of NE (NI	DEQ, 2008)	1 in 5 W	er jakt va s	#H -0-66
NE SBB1BBLUE110	111111111111111111111111111111111111111	1.558	2.965		
NE SBB1BBLUE275		2.066	2.81	4 4 4	LITE
NE SBB2TRKEY110		1.968	5.635		
NE SBB3WFBBR160	is Marie 1818	0.968	2.793		- 12
NE SBB4BBLUE411		4.006	4.867	6.921	
NE SBB4LNCLN107		1.672	2.116		A ALTON
NE SEL1ELKHR126		1.04		T. 6 (2 (3) )	
NE SEL1ELKHR235	- 17 7 10 14 2	1.022	0.631	- AF 53 -4 5	
NE SEL1MAPLEC15		1.988	0.534		· Lighte
NE SEL1PEBBL125		1.871	0.532		. Testing of
NE SLB1LBLUE000	. Schaphere	2.37	3.061	127	-
NE SLB2BSNDY165	, T	2.715	4.472		- 4-1
NE SLB2LBLUE290		1.874	2.391	1.572	35 44
NE SLO1BEAVR114	10 12 7 4 -	4.318	11.17		
NE SLO1CEDAR109		2.5	-0-	-01.1	
NE SLO1LOUPC150	77 - 6	3.45.7	0.903	- (A)	
NE SLO3MLOUP128		1.546	2.845		Mary -
NE SLO4MUDCR133	riging points in .	3.129	1.129		
NE SLO4SLOUP135		2.291	75 75 2	1-1-	The Late
NE SLP1ANTLP104		J	0.83		- N-A

Site	2003	2004	2005	2006	2007
NE SLP1PLATT150		1.265	0.685		
NE SLP1PLATT260	the Contract	1.099	1.388	72 TA 7	15-
NE SLP1SHELL207	- 7/-2	0.842	2.065	2.138	E 3
NE SLP2LSALTC08		0.703	1.349	7 7 2	
NE SLP2LSALTC108	17		0.955		
NE SLP2LSALTC301	The second P		0.971		
NE SLP2MIDDL150		0.863	3.07.	4 = 1 = 1 = 1	
NE SLP2OAKCK173	1 - 0	0.468	. 10 1 10 1		
NE SLP2SALT301		0.100		1.168	
NE SLP2WAHOO107		1.153	1.292		
NE SMP1PLATT225			1.174		
NE SMP2PLATT133		-0 V 1	37	1.512	
NE SMP2WOODR225			0.887		
NE SNE1WPNGW135	9.9.11	7. 73	0.925	7 72 1172	_
NE SNE2BIGNEM60		0.933	1.365		_
NE SNE2MUDDY173		0.823	1.505		
NE SNE2NFBNE215	3 4 1	0.55			
NE SNE2NFBNR152		0.631	1.028	1.037	£
NE SNE2SFBNE105	-:	0.935	1.020	1.037	
NE SNE3LNEMA143		1.095	1.435	217.53	
	ate of MN (M		1.433		
MN Middle Branch of the	ate of wild (w	0.664			
Whitewater River		0.004	7 7		
	(FIFRA SAP	2008: Lero	h 2008)		
USDA Goodwater Creek	1.478	2.63	2.347	2.825	1,1439
CWS - A	Atrazine Mor	itoring Prog		- 2 /	
AMP OH-16	1 11/15	9 25 0	1.822		
AMP OH-04	a market		3.864		
AMP-IL-29	i u I		0.951	-1,	1.078
AMP-IL-23	· January .		2	E	1.176
AMP-IL-22	1 3- 1 1 12 W	14 · 34	1.56	A,D ,3 , =	0.796
AMP-IN-10			2.253		
AMP-KS-16	1 1 2 2 2 1 L	-3-11	2.084	V	581 4 6
AMP-MO-16		- 1775	2.221	14.1141	
H	eidelberg Co	llege (OH)		5 (5 5 5	. 1116163
Honey Creek (1996-1999)	1.05	1.25	0.99	1.72	
Honey Creek (2000-2002)	0.69	0.52	1.87	-5 mi-5.m	
Maumee (1996-98, 2000-01)	0.79	1.44	0.97	0.57	0.90
Miami (1996-98, 2000-01)	0.28	1.11	0.39	0.41	0.52
Musk (1996-98, 2000-01)	0.32	0.37	0.19	0.10	0.33
Raisin (1996-98, 2000-01)	0.35	1.71	0.20	0.21	0.49
Rock (1996-98, 2000-01)	0.61	1.14	0.76	0.49	0.50
Sandusky (1995-2000)	0.87	0.98	1.57	1.056	0.57
Scioto (1996-2001)	0.69	1.33	0.55	0.32	0.78

## 2. Evaluating Vulnerable Watersheds With Monitoring Sites Not in the AEEMP

As a first step in evaluating the watershed criteria, US EPA overlaid the locations of the monitoring sites described in Section VI.D.1 onto the distribution of watersheds that met the precipitation, atrazine use intensity, and soil criteria described in Section VI.C and shown in Figure VI-10. The Agency used GIS tools to evaluate how many of the non-AEEMP sites that exceeded the PATI LOC<sub>MEI</sub> (Table VI-2) were located in catchments that met the criteria for precipitation (annual average >23 inches), atrazine use intensity (≥0.1 lb ai/A), and drainage-restrictive soils (>60% hydrologic group C or D soils and >45% of soils with a Ksat of <1 um/s within 50 cm of the surface). Half of the sites that exceeded the LOC in one or more years in the NDEQ, MO USDA ARS, and AMP CWS monitoring data occur in areas that meet all of the criteria for watersheds that are similar to AEEMP sites that exceeded the LOC in multiple years (Table VI-3). While none of the Heidelberg College sites are located in watersheds that meet the soil ctiteria, the results of these sites also reflect earlier use patterns (primarily from 1996 to 2001).

Table VI-3 Preliminary Evaluation of Sites Not in the AEEMP That Exceeded the PATI LOC<sub>MEI</sub>

Monitoring Data Set	LOC Criteria	Total Sites	Sites meeting the criteria for:				
			Precipi- tation <sup>1</sup>	Precip + Use 2	Soils <sup>3</sup>	Precip + Use + Soils	
Nebraska DEQ (NDEQ)	Exceeds LOC multiple years	14	14	14	5	5	
	Exceeds 1 yr	12	12	12	8	8	
	% of exceeding sites	100%	100%	`00\$	50%	50%	
Missouri USDA ARS	Exceeds LOC multiple years	1	1	1	1	1	
	% of exceeding sites	100%	100%	100%	100%	100%	
Minnesota DA	Exceeds LOC	0	0	0	0	0	
	% of exceeding sites	na	na	na	na	na	
Heidelberg College (OH)	Exceeds LOC multiple years	2	2	2	0	0	
	Exceeds 1 yr	5	5.	5	0	0	
	% of exceeding sites	100%	100%	100%	0%	0%	
AMP CWS	Exceeds LOC	8	8	6	5	4	
	% of exceeding sites	100%	100%	75%	62.5%	50%	
Kansas	>20 ug/L	25	25	14	11	5	
	% of high detect sites	100%	100%	56%	44%	20%	

The Agency plans additional analyses of all of these monitoring sites, including a breakdown of the monitoring sties by size of the upstream catchment and an evaluation of the upstream catchment characteristics of selected monitoring sites. US EPA will provide these updated results during the May 2009 SAP meeting.

<sup>&</sup>lt;sup>1</sup> Catchments with annual average precipitation >23 inches.

<sup>&</sup>lt;sup>2</sup> Atrazine use intensity ≥0.1 lb ai per catchment acre
<sup>3</sup> At least 60 percent of the upstream catchment area consisted of hydrologic group C or D soils and at least 45 percent of the soils in the catchment area had a subsurface layer with a Ksat of <1 um/s within 50 cm of the surface.

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